Supporting Information For:

Catalytic Hydrothiolation: Counter-ion Controlled Regioselectivity

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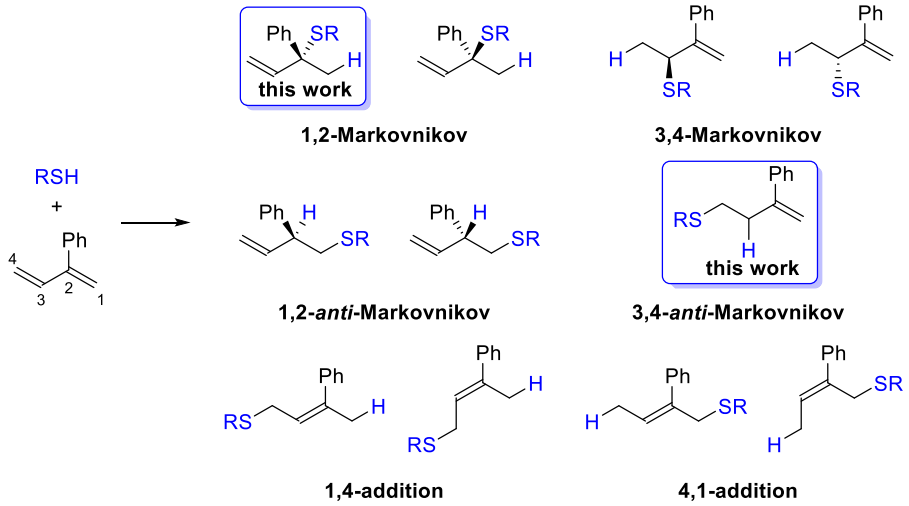
1. General:

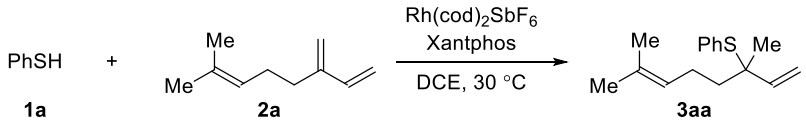
Commercial reagents were purchased from Sigma Aldrich, Strem, Alfa Aesar, Acros Organics or TCI and used without further purification. 1,2-Dichloroethane, 1,4-dioxane, methanol and ethanol were purified using an Innovative Technologies Pure Solv system, degassed by three freeze-pump-thaw cycles, and stored over 3Å MS within a N_2 filled glove box. All experiments were performed in oven-dried or flame-dried glassware. Reactions were monitored using either thin-layer chromatography (TLC) or gas chromatography using an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Purification and isolation of products were performed via silica gel chromatography (both column and preparative thinlayer chromatography). Column chromatography was performed with Silicycle Silica-P Flash Silica Gel using glass columns. Solvents were purchased from Fisher. ^{1}H NMR, ^{2}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on Bruker CRYO500 or DRX400 spectrometer. ^{1}H NMR spectra were internally referenced to the residual solvent signal or TMS. ^{13}C NMR spectra were internally referenced to the residual solvent signal. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. Data for ^{2}H NMR, ^{13}C NMR, and ^{31}P NMR are reported in terms of chemical shift (δ ppm). Infrared (IR) spectra were obtained on a Nicolet iS5 FT-IR spectrometer with an iD5 ATR and are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were obtained on a micromass 70S-250 spectrometer (EI) or an ABI/Sciex QStar Mass Spectrometer (ESI). Enantiomeric excesses for enantioselective reactions were determined by chiral SFC analysis using an Agilent Technologies HPLC (1200 series) system and Aurora A5 Fusion. 1,3-Dienes **2e-2g** used here were known compounds and synthesized according to the reported methods.[1]

2. Possible isomers for the hydrothiolation of unsymmetric 1,3-diene



3. Mechanism studies for 1,2-Markovnikov hydrothiolation

3.1 Kinetic studies



The kinetic profile of the reaction was studied by obtaining initial rates of the reaction with different concentrations of thiophenol (**1a**), myrcene (**2a**), and Rh-catalyst. No products of decomposition are observed for the system. The rates were monitored by GC-FID analysis using 1,3,5-trimethoxybenzene as an internal standard.

Determination of the reaction order in catalyst

Representative procedure (entry 1):

In a N_2-filled glove box, a 0.08M catalyst solution was prepared by combining $Rh(cod)_2SbF_6$ (44.4 mg, 0.08 mmol), Xantphos (46.3 mg, 0.08 mmol), and DCE (1.0 mL). A solution of reagents was prepared by combining **1a** (55.1 mg, 0.50 mmol), **2a** (102.1 mg, 0.75 mmol), and DCE (1.0 mL). A vial was charged with a stir bar and 1,3,5-trimethoxybenzene (6.0 mg, 0.036 mmol). Next, 0.05 mL of catalyst solution was added to the vial, followed by 0.2 mL of reagent solution. Additional DCE was added to the vial to make the total reaction volume 0.4 mL, and the vial was sealed with a Teflon cap. Aliquots (10 µL) were taken every 5 minutes and quenched with 2 mL of EtOAc. The reaction halts in EtOAc. The amount of **3aa** was monitored by GC-FID analysis.

Table S1. Observed rate versus catalyst concentration for 1,2-Markovnikov hydrothiolation

entry	1	2	3	4
[Rh] (M)	0.01	0.02	0.03	0.04
k_{obs} (M/min)	1.44×10^{-4}	3.09×10^{-4}	3.89×10^{-4}	5.62×10^{-4}

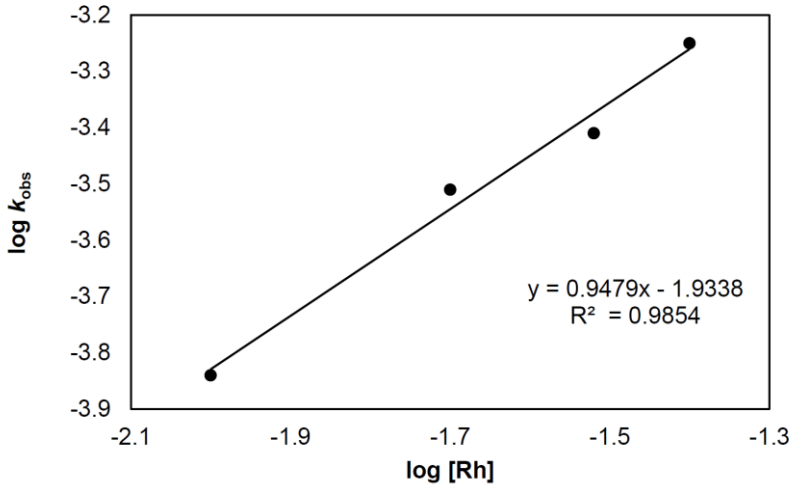


Figure S1. Plot of logk_{obs} vs log[Rh] for 1,2-Markovnikov hydrothiolation (first order)

Determination of the reaction order in myrcene (2a)

Representative procedure (entry 1):

In a N_2-filled glove box, a 0.025M catalyst solution was prepared by combining $Rh(cod)_2SbF_6$ (27.8 mg, 0.05 mmol), Xantphos (28.9 mg, 0.05 mmol), and DCE (2.0 mL). A solution of **1a** (110.2 mg, 1.0 mmol) in DCE (2.0 mL) was prepared. A vial was charged with a stir bar, 1,3,5-trimethoxybenzene (6.0 mg, 0.036 mmol), and **2a** (13.6 mg, 0.1 mmol). Catalyst solution (0.2 mL) was added to the vial, followed by 0.2 mL of **1a** solution, and the vial was sealed with a Teflon cap. Aliquots (10 µL) were taken every 5 minutes and quenched in 2 mL of EtOAc. The reaction halts in EtOAc. The amount of **3aa** was monitored by GC-FID analysis.

Table S2. Observed rate versus myrcene **(2a)** concentration for 1,2-Markovnikov hydrothiolation

entry	1	2	3	4	5
[**2a**] (Initial) (M)	0.25	0.5	0.75	1.0	1.25
k_{obs} (M/min)	1.01×10^{-4}	1.04×10^{-4}	1.05×10^{-4}	1.03×10^{-4}	1.09×10^{-4}

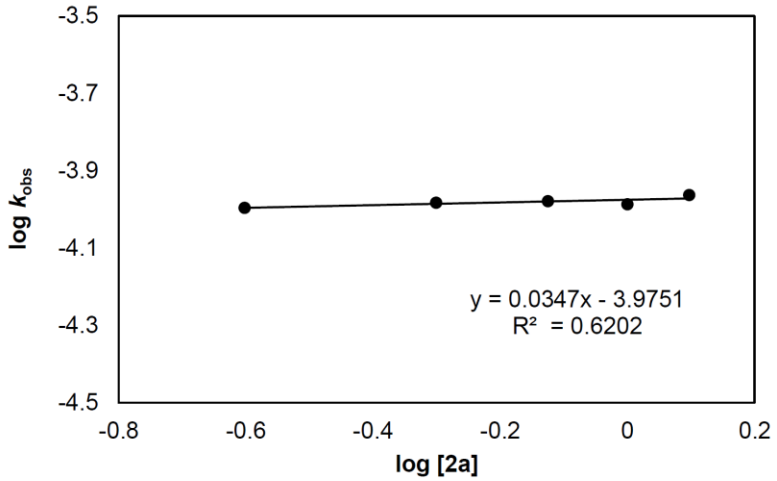


Figure S2. Plot of logk_{obs} vs log[**2a**] for 1,2-Markovnikov hydrothiolation (zero order)

Determination of the reaction order in thiophenol (1a)

Representative procedure (entry 1):

In a N_2-filled glove box, a 0.025M catalyst solution was prepared by combining $Rh(cod)_2SbF_6$ (13.9 mg, 0.025 mmol), Xantphos (14.5 mg, 0.025 mmol), and DCE (1.0 mL). A solution of **2a** (102.2 mg, 0.75 mmol) in DCE (1.0 mL) was prepared. A vial was charged with a stir bar, 1,3,5-trimethoxybenzene (6.0 mg, 0.036 mmol) and **1a** (11.0 mg, 0.1 mmol). Catalyst solution (0.2 mL) was added to the vial, followed by 0.2 mL of **2a** solution, and the vial was sealed with a Teflon cap. Aliquots (10 µL) were taken every 5 minutes and quenched in 2 mL of EtOAc. The reaction halts in EtOAc. The amount of **3aa** was monitored by GC-FID analysis.

Table S3. Observed rate versus thiophenol **(1a)** concentration for 1,2-Markovnikov hydrothiolation

entry	1	2	3	4
[**1a**] (Initial) (M)	0.25	0.5	1.0	1.25
k_{obs} (M/min)	1.32×10^{-4}	1.78×10^{-4}	2.18×10^{-4}	2.45×10^{-4}

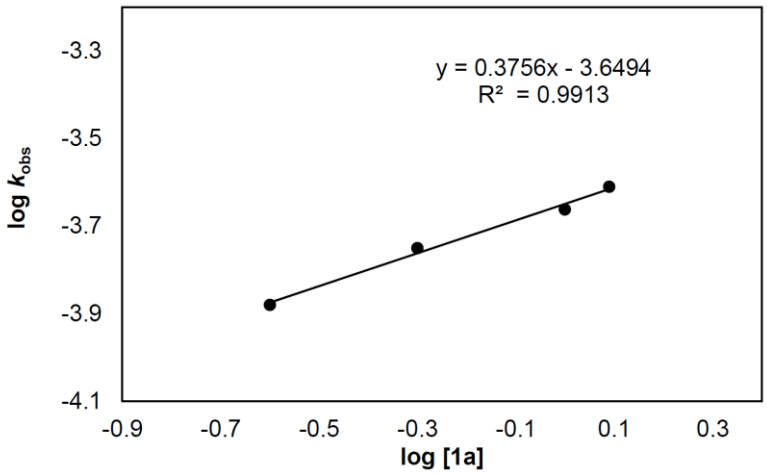


Figure S3. Plot of logk_{obs} vs log[**1a**] for 1,2-Markovnikov hydrothiolation (fractional order: 0.4)

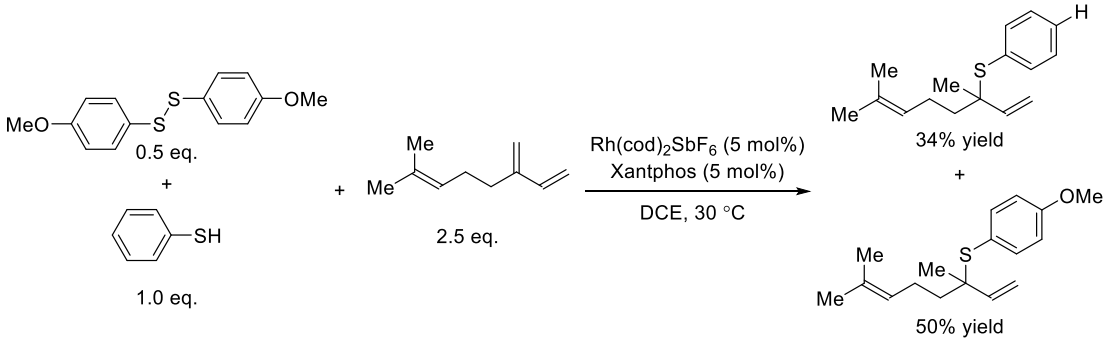


Figure S4. Compete reaction between disulfide and thiophenol.

3.2 Deuterium-labeling studies

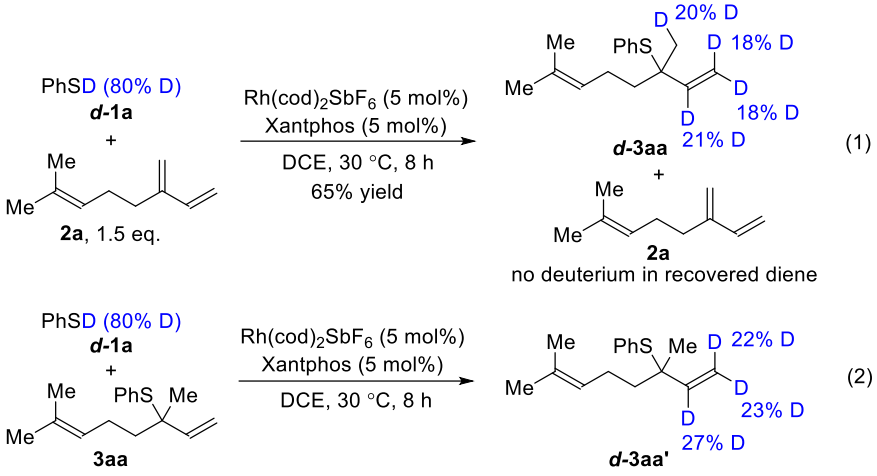


Figure S5. Deuterium-labeling studies for 1,2-Markovnikov hydrothiolation

In a N_2-filled glovebox, Xantphos (2.9 mg, 0.005 mmol) and DCE (0.40 mL) were added to a 1-dram vial containing $Rh(cod)_2SbF_6$ (2.8 mg, 0.005 mmol). The resulting mixture was stirred for 10 min and then myrcene (**2a**, 20.4 mg, 0.15 mmol, in eq.1) or **3aa** (24.6 mg, 0.1 mmol, in eq.2), and thiol ***d*-1a** (11.0 mg, 0.10 mmol) were added. The mixture was held at 30 °C until no starting material was observed by TLC. The resulting mixture was then cooled to rt. The regioselectivities were determined by ^1H NMR analysis of the unpurified reaction mixture. The product was purified by preparative thinlayer chromatography (hexanes/EtOAc = 40/1). **^1H NMR** for ***d*-3aa** (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.34 – 7.26 (m, 3H), 5.94 – 5.85 (m, 0.79H), 5.12 – 5.04 (m, 1H), 5.00 – 4.92 (m, 0.82H), 4.75 – 4.66 (m, 0.82H), 2.18 – 1.96 (m, 2H), 1.68 (s, 3H), 1.65 – 1.59 (m, 5H), 1.31 (s, 2.8H).

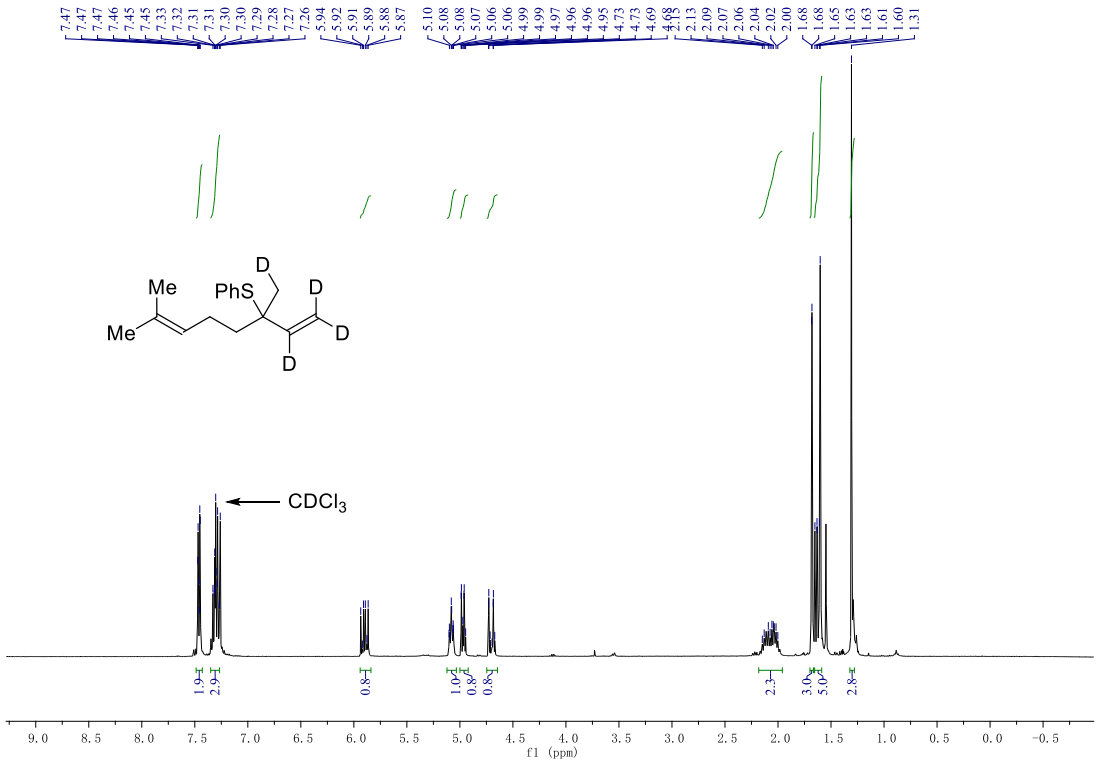


Figure S6. ^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)] for ***d*-3aa**

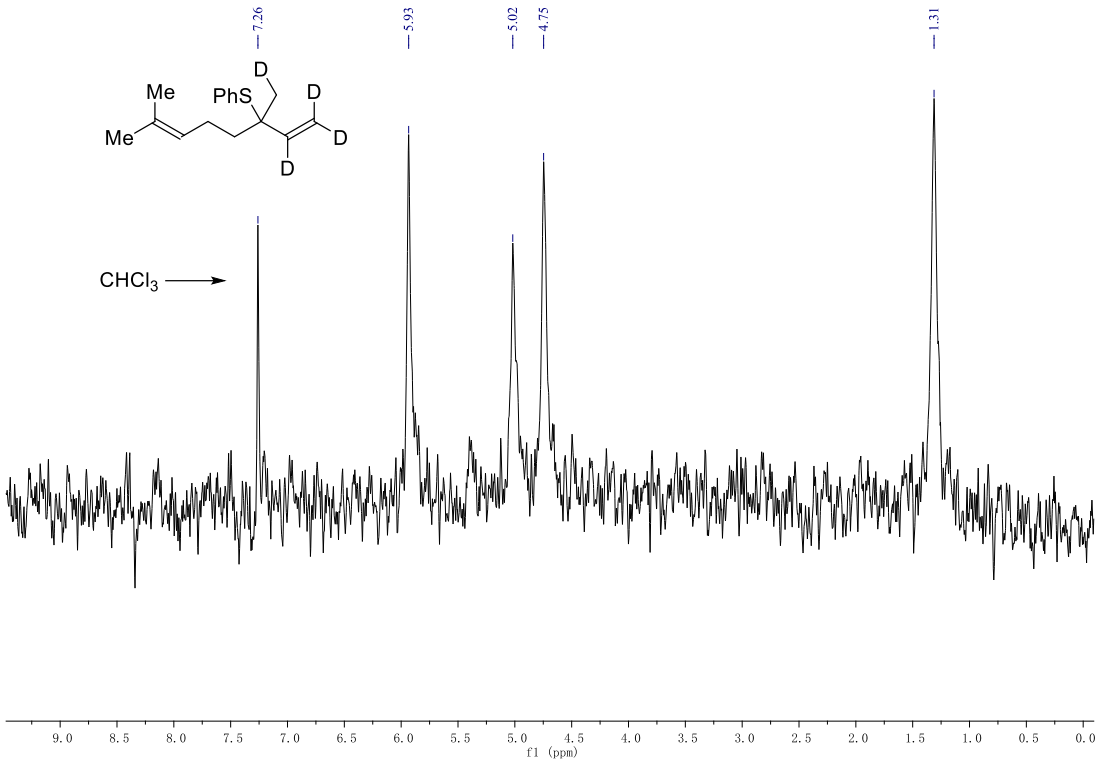


Figure S7. ^{2}H NMR [400 MHz, $CHCl_3$ (δ 7.26 ppm)] for ***d*-3aa**

3.3 NMR studies

In a N_2-filled glovebox, Xantphos (5.8 mg, 0.01 mmol) and DCE-d_4 (0.50 mL) were added to a 1-dram vial containing $Rh(cod)_2SbF_6$ (5.6 mg, 0.01 mmol). The resulting mixture was stirred for 10 min and then thiophenol (**1a**, 11.0 mg, 0.10 mmol) was added. The reaction mixture was transferred to a J. Young NMR tube to perform ^{1}H NMR and ^{31}P NMR spectroscopy. A resonance at −13.5 ppm was observed in less than ten minutes at rt in the ^{1}H NMR spectrum (Figure S8) and an equivalent phosphine resonance in the ^{31}P NMR spectrum [doublet (δ = 30.3 ppm, $J_{Rh–P}$ = 108 Hz)] was observed (Figure S9). Myrcene (**2a**, 13.6 mg, 0.1 mmol) was then added to this mixture, and the Rh–H resonance disappeared and a new complex with non-equivalent phosphine resonances was formed [a pair of doublet of doublet signals (δ = 26.6 ppm, $J_{Rh–P}$ = 174 Hz, $J_{P–P}$ = 8 Hz; δ = 16.0 ppm, $J_{Rh–P}$ = 115 Hz, $J_{P–P}$ = 8 Hz)] (Figure S10). When we subjected the product **3aa** (24.6 mg, 0.10 mmol) to a mixture of $Rh(cod)_2SbF_6$ (5.6 mg, 0.01 mmol) and Xantphos (5.8 mg, 0.01 mmol) in DCE-d_4, we observed the same species by ^{31}P NMR spectroscopy (Figure S11). Based on these results and the kinetic studies, we labeled rhodium intermediate **IV** as the resting state in the catalytic cycle (Figure 3).

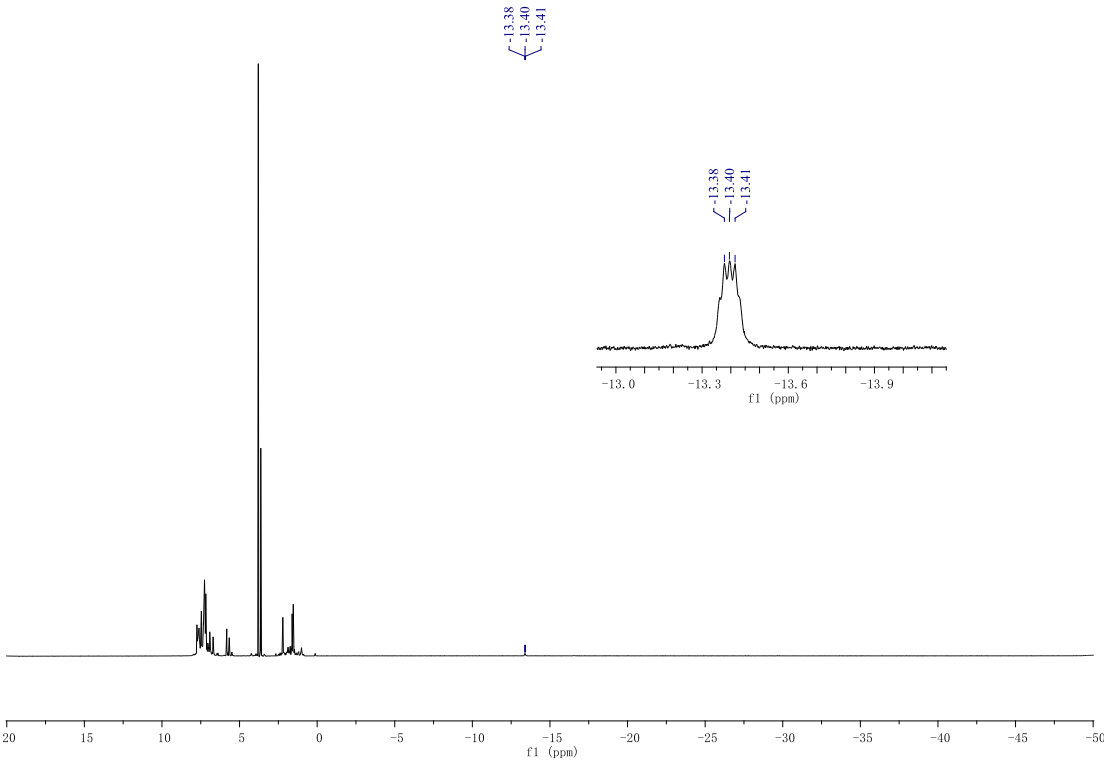


Figure S8. ^{1}H NMR (500 MHz) for a mixture of Rh(Xantphos)SbF_6 and thiophenol (**1a**) in DCE-d_4 (δ 3.79 ppm)

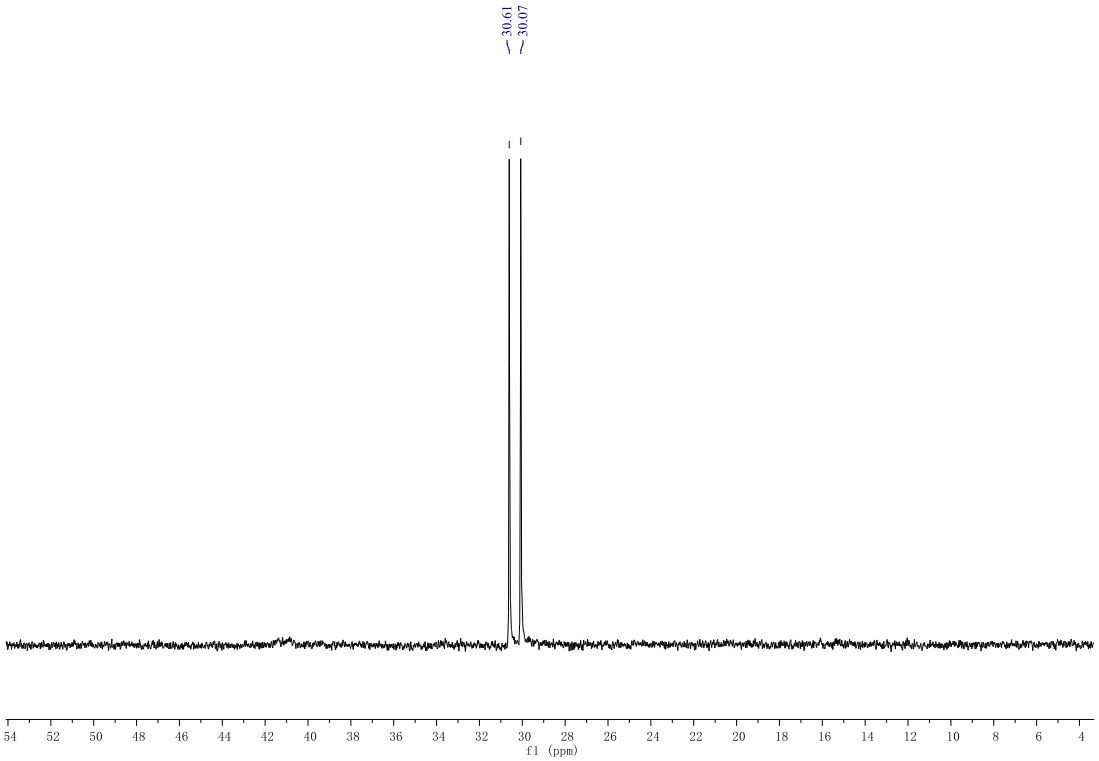


Figure S9. ^{31}P NMR (202 MHz) for a mixture of Rh(Xantphos)SbF_6 and thiophenol (**1a**) in DCE-d_4

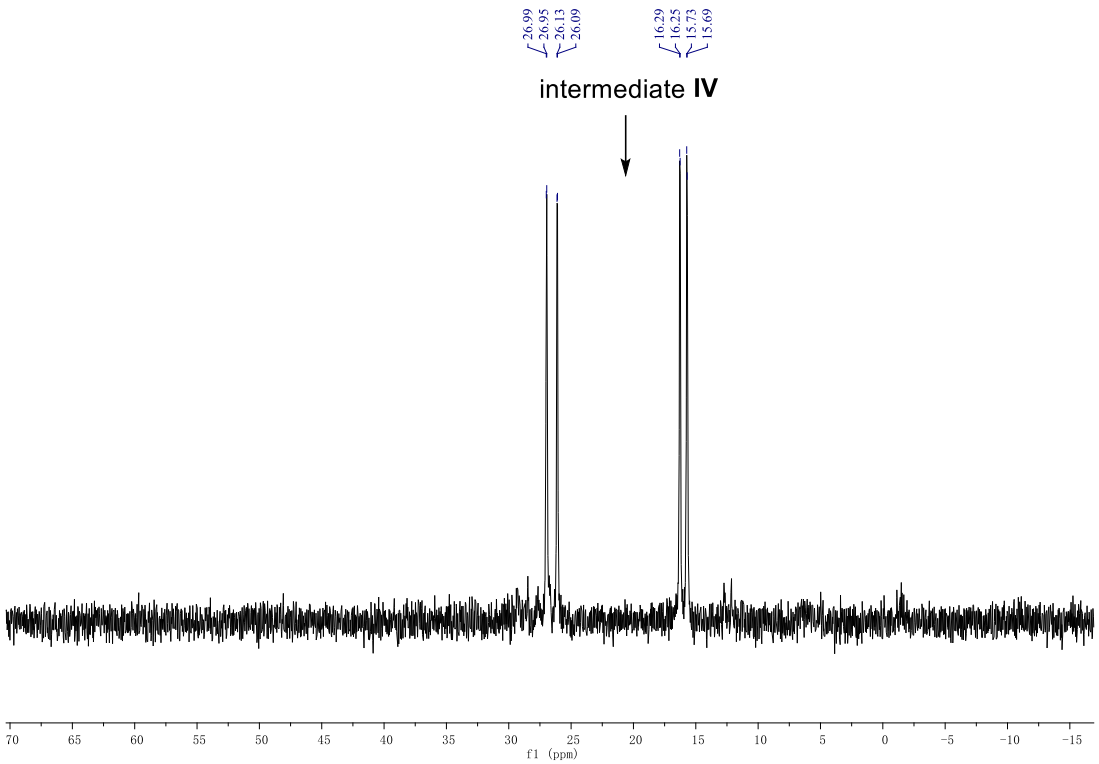


Figure S10. ^{31}P NMR (202 MHz) for a mixture of Rh(Xantphos)SbF_6, thiophenol (**1a**), and myrcene (**2a**) in DCE-d_4

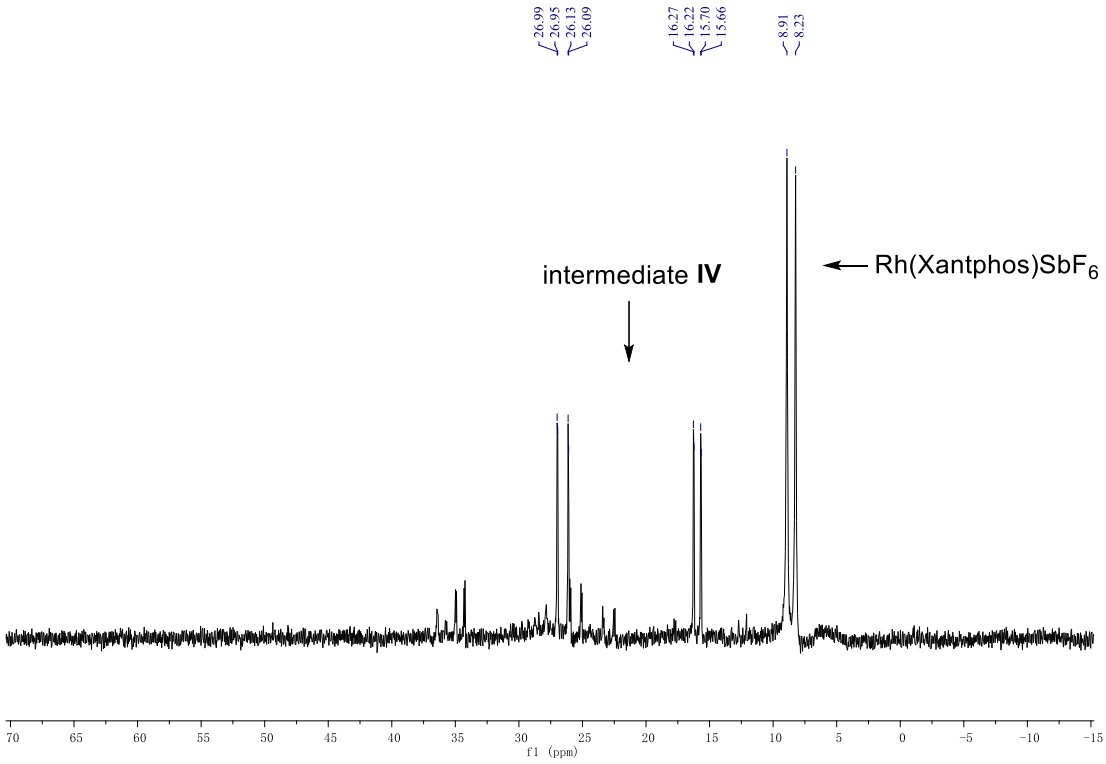
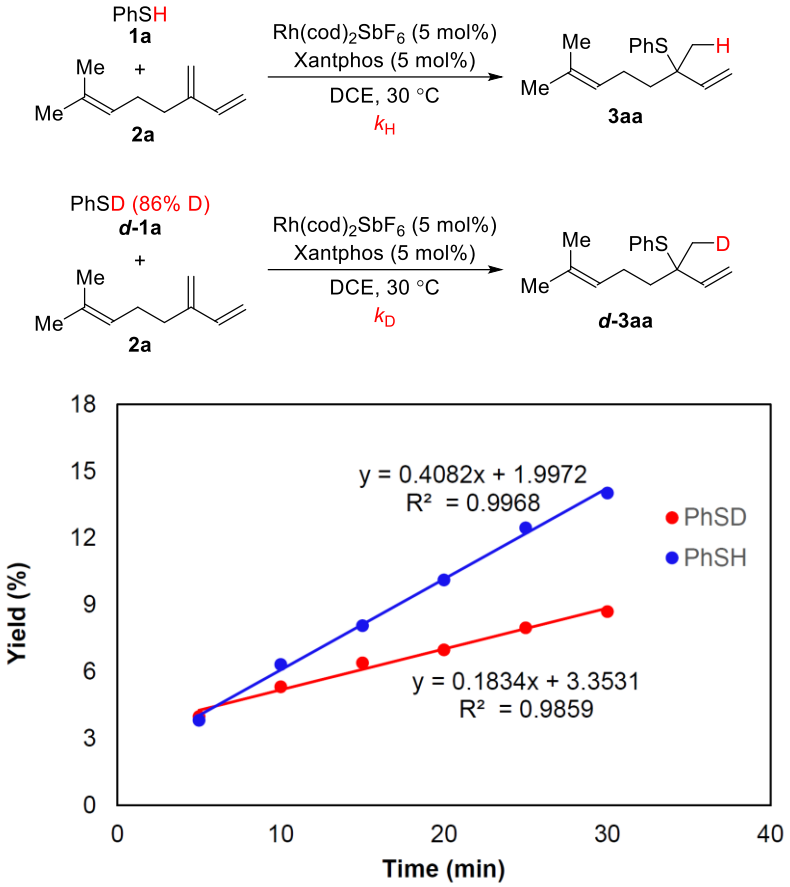


Figure S11. ^{31}P NMR(202 MHz) for a mixture of Rh(Xantphos)SbF_6 and **3aa** in DCE-d_4

3.4 Initial rate *KIE* study

In a N_2-filled glove box, a 0.025M catalyst solution was prepared by combining $Rh(cod)_2SbF_6$ (13.9 mg, 0.025 mmol), Xantphos (14.5 mg, 0.025 mmol), and DCE (1.0 mL). A solution of **2a** (102.2 mg, 0.75 mmol) in DCE (1.0 mL) was prepared. A vial was charged with a stir bar, 1,3,5-trimethoxybenzene (6.0 mg, 0.036 mmol), and then **1a** (11.0 mg, 0.1 mmol) or ***d*-1a** (11.1 mg, 0.1 mmol) were added. Catalyst solution (0.2 mL) was added to the vial, followed by 0.2 mL of **2a** solution, and the vial was sealed with a Teflon cap. Aliquots (10 µL) were taken every 5 minutes and quenched in 2 mL of EtOAc. The reaction halts in EtOAc. The amount of **3aa** was monitored by GC-FID analysis.



adjusted initial rate of deutro species[2] (considering 14% PhSH):

$$0.183 = 0.86\ k_D + 0.14 \times 0.408$$

$$k_D = 0.146$$

Calculation of KIE: $k_H/k_D = 0.408/0.146 = 2.8$

Figure S12. Initial rate *KIE* for 1,2-Markovnikov hydrothiolation

3.5 Hammett plot

In a N_2-filled glove box, a 0.025M catalyst solution was prepared by combining $Rh(cod)_2SbF_6$ (13.9 mg, 0.025 mmol), Xantphos (14.5 mg, 0.025 mmol), and DCE (1.0 mL). A solution of **2a** (102.2 mg, 0.75 mmol) in DCE (1.0 mL) was prepared. A vial was charged with a stir bar, 1,3,5-trimethoxybenzene (6.0 mg, 0.036 mmol), and **1a** (5.5 mg, 0.05 mmol) and **1h** (X = OMe, 7.0 mg, 0.05 mmol). Catalyst solution (0.2 mL) was added to the vial, followed by 0.2 mL of **2a** solution, and the vial was sealed with a Teflon cap. After 30 min, the ratio of product **3aa** and **3ha** was

detected based on the crude ^{1}H NMR spectrum. The same procedure was used for the other *para*-substituted thiophenols.

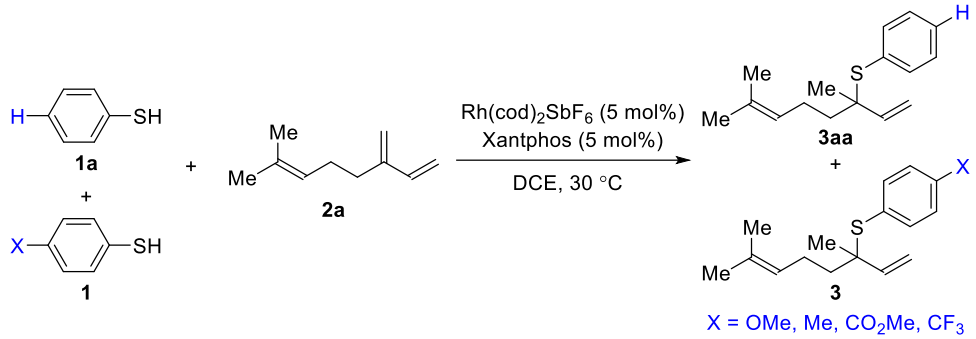


Table S4. Rate ratio versus standard σ+ for 1,2-Markovnikov hydrothiolation

entry	1	2	3	4	5
X	OMe	Me	H	CO_2Me	CF_3
σ+	-0.78	-0.31	0	0.49	0.61
k/k_H	1.64	1.16	1	0.85	0.8
log k/k_H	0.216	0.063	0	-0.071	-0.095

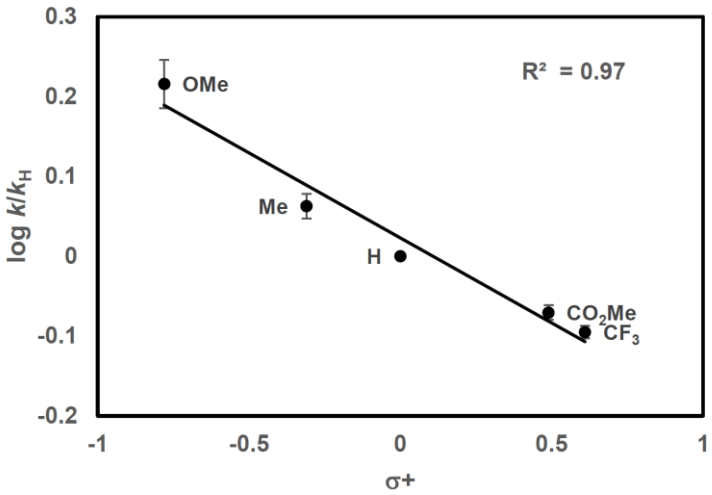
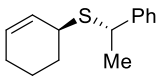


Figure S13. Hammett plot for 1,2-Markovnikov hydrothiolation (log $k/k_H = m\sigma^+ + b$ ($m = -0.22 \pm 0.02$; $b = 0.03 \pm 0.01$).

3.6. Catalyst-controlled diastereoselective hydrothiolation (for Figure 7)

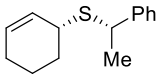
In a N_2-filled glovebox, enantioenriched Tol-BINAP (1.4 mg, 0.002 mmol) and DCE (0.80 mL) were added to a 1-dram vial containing $Rh(cod)_2SbF_6$ (1.1 mg, 0.002 mmol). The resulting mixture was stirred for 10 min and then chiral thiol **1** (0.20 mmol) and 1,3-cyclohexadiene (**2b**, 32.0 mg, 0.40 mmol) were added. The mixture was held at 30 °C until no starting material was observed by TLC. The resulting solution was then cooled to rt. The regioselectivities were determined by ^{1}H NMR analysis of the unpurified reaction mixture. Isolated yields (obtained by preparative thinlayer chromatography) are reported.

((*S*)-cyclohex-2-en-1-yl)((*S*)-1-phenylethyl)sulfane ((*S*,*S*)-3cb)



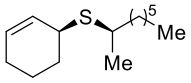
Colorless oil, 83% yield, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_D$ = -283.9 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.20 (m, 1H), 5.76 – 5.70 (m, 2H), 4.06 (q, *J* = 7.0 Hz, 1H), 3.21 – 3.13 (m, 1H), 2.03 – 1.90 (m, 2H), 1.80 – 1.70 (m, 2H), 1.63 – 1.45 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.6, 129.1, 128.6, 128.1, 127.4, 127.1, 44.0, 40.2, 29.5, 25.0, 23.2, 20.1. **IR** (ATR): 2923, 1490, 1451, 1054, 1026, 871, 751 cm^{-1}. **HRMS** calculated for $C_{14}H_{18}S$ $[M]^+$ 218.1129, found 218.1134.

((*R*)-cyclohex-2-en-1-yl)((*S*)-1-phenylethyl)sulfane ((*R*,*S*)-3cb)



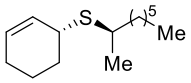
Colorless oil, 87% yield, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_D$ = -68.8 (*c* 0.4, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.34 – 7.29 (m, 2H), 7.25 – 7.20 (m, 1H), 5.72 – 5.67 (m, 1H), 5.48 – 5.42 (m, 1H), 4.02 (q, *J* = 7.1 Hz, 1H), 3.06 – 2.98 (m, 1H), 2.04 – 1.90 (m, 2H), 1.90 – 1.73 (m, 3H), 1.60 –1.51 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.7, 129.7, 128.7, 127.6, 127.5, 127.2, 43.7, 40.1, 29.3, 25.1, 23.1, 19.6. **IR** (ATR): 2924, 1490, 1451, 1054, 1026, 871, 751 cm^{-1}. **HRMS** calculated for $C_{14}H_{18}S$ $[M]^+$ 218.1129, found 218.1128.

((*S*)-cyclohex-2-en-1-yl)((*R*)-octan-2-yl)sulfane ((*S*,*R*)-3db)



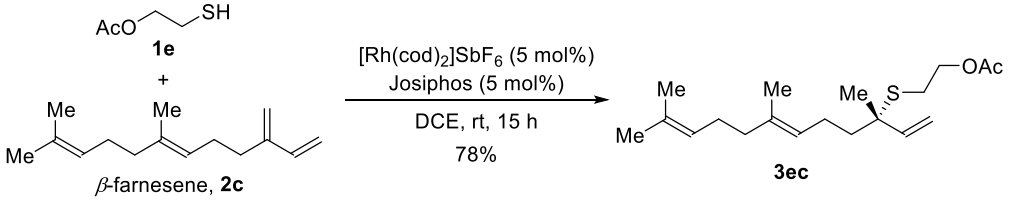
Colorless oil, 92% yield, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_D$ = -160.0 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.78 – 5.67 (m, 2H), 3.43 – 3.35 (m, 1H), 2.89 – 2.77 (m, 1H), 2.03 – 1.93 (m, 3H), 1.90 – 1.79 (m, 1H), 1.78 – 1.69 (m, 1H), 1.65 – 1.53 (m, 3H), 1.52 – 1.36 (m, 3H), 1.33 – 1.23 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.0, 128.6, 39.9, 39.6, 37.8, 32.0, 30.4, 29.5, 27.1, 25.1, 22.8, 22.0, 20.2, 14.3. **IR** (ATR): 2954, 2924, 2855, 1455, 1374, 1202, 1036, 986, 870 cm^{-1}. **HRMS** calculated for $C_{14}H_{26}S$ $[M]^+$ 266.1755, found 266.1751.

((*R*)-cyclohex-2-en-1-yl)((*R*)-octan-2-yl)sulfane ((*R*,*R*)-3db)



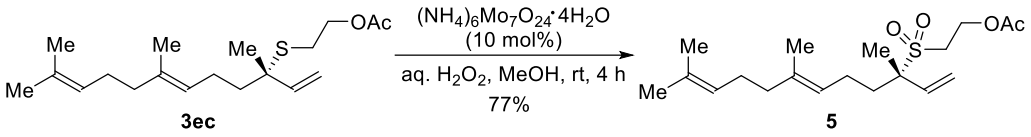
Colorless oil, 90% yield, >20:1 *dr*, >20:1 *rr*, $[\alpha]^{24}_D$ = +145.6 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.79 – 5.73 (m, 1H), 5.72 – 5.66 (m, 1H), 3.44 – 3.35 (m, 1H), 2.87 – 2.75 (m, 1H), 2.05 – 1.81 (m, 4H), 1.79 – 1.69 (m, 1H), 1.66 – 1.36 (m, 6H), 1.34 – 1.24 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.3, 128.4, 39.7, 39.4, 37.5, 32.0, 30.2, 29.4, 27.2, 25.1, 22.8, 22.3, 19.8, 14.3. **IR** (ATR): 2954, 2924, 2855, 1455, 1374, 1203, 995, 870 cm^{-1}. **HRMS** calculated for $C_{14}H_{26}S$ $[M]^+$ 266.1755, found 266.1757.

4. Total synthesis of (–)-agelasidine A

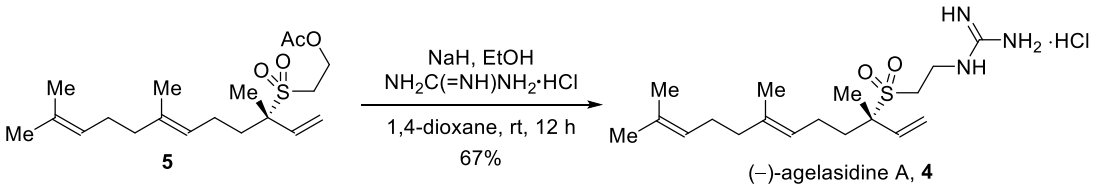


In a N_2-filled glovebox, Josiphos (27.7 mg, 0.05 mmol) and DCE (4.0 mL) were added to a 20 mL vial containing $Rh(cod)_2SbF_6$ (27.8 mg, 0.05 mmol). The resulting mixture was stirred for 10 min and then 1,3-diene **2c** (306.6 mg, 1.5 mmol) and thiol **1e** (120.2 mg, 1.0 mmol) were added. The mixture was held at 30 °C for 12 h. DCE was removed under reduced pressure and the pure sulfide **3ec** was obtained after column chromatography (hexanes/ EtOAc = 5/1) as a colorless oil

(252.9 mg, 78% yield, >99:1 *er*, >20:1 *rr*). $[\alpha]^{24}_D$ = +8.2 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.79 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.16 – 5.05 (m, 3H), 4.98 (d, *J* = 17.4 Hz, 1H), 4.14 (t, *J* = 7.1 Hz, 2H), 2.63 – 2.56 (m, 2H), 2.10 – 1.94 (m, 9H), 1.68 (s, 3H), 1.63 – 1.56 (m, 8H), 1.36 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.0, 143.5, 135.8, 131.6, 124.5, 123.9, 113.0, 64.2, 50.7, 40.6, 39.8, 27.5, 26.9, 25.9, 23.7, 23.3, 21.1, 17.9, 16.2. **IR** (ATR): 2966, 2922, 1743, 1449, 1377, 1226, 1026, 997, 913 cm^{-1}. **HRMS** calculated for $C_{19}H_{33}O_2S$ $[M+H]^+$ 325.2201, found 325.2206. **Chiral SFC**: 250 mm CHIRALCEL IC, 2.0% ^{i}PrOH, 3.0 mL/min, 220 nm, 44 °C, nozzle pressure = 200 bar CO_2, t_{R1} (minor) = 5.7 min, t_{R2} (major) = 6.1 min.



Based on the literature,[3] $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (90.2 mg, 0.073 mmol) and H_2O_2 (328.7 mg, 2.9 mmol, 30 wt% aqueous solution) were added to a solution of **3ec** (237.0 mg, 0.73 mmol) in MeOH (2 mL). The reaction mixture was stirred for 4 h at rt. MeOH was evaporated and the crude mixture was washed with *aq*. $NaHCO_3$ and extracted with Et_2O. The Et_2O was evaporated and followed by column chromatography (hexanes/ EtOAc = 3/1) to obtain the pure sulfone **5** as a colorless oil (200.4 mg, 77% yield). $[\alpha]^{24}_D$ = +12.4 (*c* 1.0, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.00 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.51 (d, *J* = 10.8 Hz, 1H), 5.39 (d, *J* = 17.6 Hz, 1H), 5.12 – 5.02 (m, 2H), 4.50 (t, *J* = 6.6 Hz, 2H), 3.24 (t, *J* = 6.6 Hz, 2H), 2.10 – 1.88 (m, 11H), 1.67 (s, 3H), 1.59 (s, 3H), 1.57 (s, 3H), 1.50 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.8, 136.7, 135.7, 131.7, 124.3, 122.8, 120.8, 68.3, 57.1, 45.8, 39.8, 31.8, 26.7, 25.8, 22.2, 20.9, 17.8, 16.2, 16.1. **IR** (ATR): 2918, 1743, 1453, 1364, 1292, 1228, 1136, 1044, 933 cm^{-1}. **HRMS** calculated for $C_{19}H_{32}O_4S$ $[M]^+$ 356.2021, found 356.2029.



Following the reported procedure,[4] sodium hydride (268.8 mg, 11.2 mmol) was treated with EtOH (8 ml) at 0 °C under a nitrogen atmosphere. To this solution was added guanidine hydrochloride (1.07 g, 11.2 mmol) at rt. After the mixture was stirred for 1 h, a white precipitate was observed. The solution was filtered and then concentrated under reduced pressure. The resulting guanidine was dissolved in a mixture of 1,4-dioxane (4 mL) and water (4 mL). The solution was cooled to 0 °C and a solution of compound **5** (100 mg, 0.28 mmol) in 1,4-dioxane (4 mL) was added dropwise over the course of 1 h. The cooling bath was removed, and the mixture was stirred for 12 h. 1,4-Dioxane was evaporated off and water was added to the residual oil. The aqueous layer was neutralized with 6 N hydrochloric acid and then extracted with DCM. The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The residual oil was purified by column chromatography (DCM/MeOH = 3/1) to obtain (–)-agelasidine A hydrogen chloride salt (73.5 mg, 67%) as a white solid. $[\alpha]^{24}_D$ = +18.6 (*c* 1.0, MeOH). [lit:[5] $[\alpha]^{24}_D$ = +19.1 (*c* 1.0, MeOH)] **^{1}H NMR** (500 MHz, CD_3OD) δ 6.01 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.58 (d, *J* = 10.8 Hz, 1H), 5.50 (d, *J* = 17.5 Hz, 1H), 5.14 (t, *J* = 6.4 Hz, 1H), 5.11 – 5.05 (m, 1H), 4.85 (brs, 5H), 3.72 (t, *J* = 6.1

Hz, 2H), 3.34 – 3.28 (m, 3H), 2.13 – 1.81 (m, 8H), 1.67 (s, 3H), 1.60 (s, 6H), 1.53 (s, 3H). **^{13}C NMR** (126 MHz, CD_3OD) δ 158.6, 137.4, 136.4, 132.3, 125.3, 124.3, 122.0, 69.2, 46.4, 40.7, 35.8, 33.1, 27.6, 25.9, 23.1, 17.8, 16.3, 16.0. **IR** (ATR): 3337, 2922, 1627, 1449, 1375, 1284, 1130, 1076, 1000, 935, 816 cm^{-1}. **HRMS** calculated for $C_{18}H_{34}N_3O_2S$ $[M]^+$ 356.2372, found 356.2387.

5. General procedure for 3,4-*anti*-Markovnikov hydrothiolation (for Table 1)

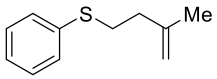
Method A:

In a N_2-filled glovebox, dppe (0.01 mmol) and DCE (0.40 mL) were added to a 1-dram vial containing $[Rh(C_2H_4)_2Cl]_2$ (0.005 mmol). The resulting mixture was stirred for 10 min, and then 1,3-diene **2** (0.40 mmol) and thiol **1** (0.20 mmol) were added. The mixture was held at 30 °C until no starting material was observed by TLC. The resulting mixture was then cooled to rt. The regioselectivities were determined by ^{1}H NMR analysis of the unpurified reaction mixture. Isolated yields (obtained by column chromatography on silica gel or preparative thinlayer chromatography) are reported.

Method B:

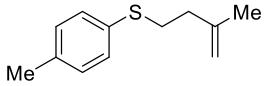
In a N_2-filled glovebox, Xantphos (0.01 mmol) and DCE (0.40 mL) were added to a 1-dram vial containing $[Rh(cod)Cl]_2$ (0.005 mmol). The resulting mixture was stirred for 10 min, and then 3,5-dimethylbenzoic acid (12 mg, 0.08 mmol), 1,3-diene **2** (0.40 mmol) and thiol **1** (0.20 mmol) were added. The mixture was held at 30 °C until no starting material was observed by TLC. The resulting mixture was then cooled to rt. The regioselectivities were determined by ^{1}H NMR analysis of the unpurified reaction mixture. Isolated yields (obtained by column chromatography on silica gel or preparative thinlayer chromatography) are reported.

(3-methylbut-3-en-1-yl)(phenyl)sulfane (6ad)[6]



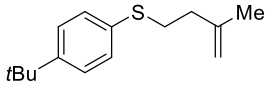
Method A, colorless oil, 94% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 4H), 7.26 – 7.22 (m, 1H), 4.87 (s, 1H), 4.82 (s, 1H), 3.10 (t, *J* = 8.0 Hz, 2H), 2.41 (t, *J* = 8.0 Hz, 2H), 1.82 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.0, 136.7, 129.2, 129.1, 126.0, 111.6, 37.4, 31.9, 22.5. **IR** (ATR): 2931, 1480, 1438, 889, 736, 689 cm^{-1}. **HRMS** calculated for $C_{11}H_{15}S$ $[M+H]^+$ 179.0894, found 179.0890.

(3-methylbut-3-en-1-yl)(*p*-tolyl)sulfane (6fd)



Method A, colorless oil, 95% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.13 – 7.07 (m, 2H), 4.79 (s, 1H), 4.74 (s, 1H), 3.02 – 2.96 (m, 2H), 2.35 – 2.30 (m, 5H), 1.76 – 1.72 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 136.3, 132.9, 130.2, 129.8, 111.5, 37.6, 32.8, 22.5, 21.2. **IR** (ATR): 2922, 1492, 1015, 889, 804 cm^{-1}. **HRMS** calculated for $C_{12}H_{17}S$ $[M+H]^+$ 193.1051, found 193.1047.

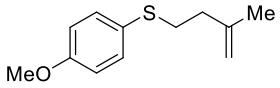
(4-(*tert*-butyl)phenyl)(3-methylbut-3-en-1-yl)sulfane (6gd)



Method A, colorless oil, 95% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 4.82 – 4.78 (m, 1H), 4.78 – 4.72 (m, 1H), 3.05 – 2.98 (m, 2H), 2.35 (t, *J* = 7.8 Hz, 2H), 1.75 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 144.1, 133.1, 129.6, 126.1, 111.5, 37.6, 34.6, 32.5, 31.5, 22.5.

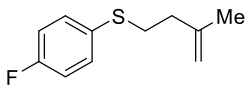
IR (ATR): 2962, 1120, 1013, 899. 819 cm^{-1}. **HRMS** calculated for $C_{15}H_{22}S$ $[M]^+$ 234.1442, found 234.1440.

(4-methoxyphenyl)(3-methylbut-3-en-1-yl)sulfane (6hd)[7]



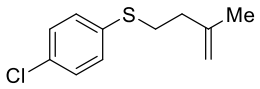
Method A, colorless oil, 68% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 6.88 – 6.81 (m, 2H), 4.78 (s, 1H), 4.71 (s, 1H), 3.80 (s, 3H), 2.97 – 2.88 (m, 2H), 2.34 – 2.25 (m, 2H), 1.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.1, 144.1, 133.4, 126.7, 114.7, 111.5, 55.5, 37.7, 34.2, 22.5. **IR** (ATR): 2914, 2360, 1510, 1247, 1174, 1034, 829 cm^{-1}. **HRMS** calculated for $C_{12}H_{16}OS$ $[M]^+$ 208.0922, found 208.0927.

(4-fluorophenyl)(3-methylbut-3-en-1-yl)sulfane (6id)



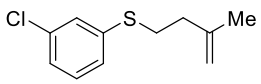
Method A, colorless oil, 82% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.03 – 6.97 (m, 2H), 4.79 (s, 1H), 4.72 (s, 1H), 3.02 – 2.93 (m, 2H), 2.30 (t, *J* = 7.7 Hz, 2H), 1.73 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.9 (d, *J* = 245.7 Hz), 143.8, 132.5 (d, *J* = 7.6 Hz), 131.5, 116.2 (d, *J* = 21.4 Hz), 111.7, 37.5, 33.4, 22.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.2. **IR** (ATR): 2933, 1589, 1489, 1225, 1156, 890, 821 cm^{-1}. **HRMS** calculated for $C_{11}H_{13}FS$ $[M]^+$ 196.0722, found 196.0713.

(4-chlorophenyl)(3-methylbut-3-en-1-yl)sulfane (6jd)



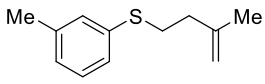
Method A, colorless oil, 93% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 4H), 4.82 (s, 1H), 4.75 (s, 1H), 3.05 – 2.99 (m, 2H), 2.34 (t, *J* = 7.7 Hz, 2H), 1.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 135.3, 132.1, 130.7, 129.2, 111.8, 37.3, 32.3, 22.4. **IR** (ATR): 2925, 2360, 1476, 1095, 1011, 891, 812 cm^{-1}. **HRMS** calculated for $C_{11}H_{13}ClS$ $[M]^+$ 212.0426, found 212.0417.

(3-chlorophenyl)(3-methylbut-3-en-1-yl)sulfane (6kd)



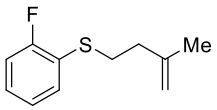
Method A, colorless oil, 91% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 1H), 7.21 – 7.17 (m, 2H), 7.16 – 7.12 (m, 1H), 4.82 (s, 1H), 4.76 (s, 1H), 3.07 – 3.00 (m, 2H), 2.35 (t, *J* = 7.7 Hz, 2H), 1.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.6, 139.1, 134.8, 130.0, 128.3, 126.8, 126.0, 111.9, 37.1, 31.6, 22.4. **IR** (ATR): 2932, 2360, 1577, 1461, 890, 778, 677 cm^{-1}. **HRMS** calculated for $C_{11}H_{13}ClS$ $[M]^+$ 212.0426, found 212.0422.

(3-methylbut-3-en-1-yl)(*m*-tolyl)sulfane (6ld)



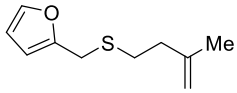
Method A, colorless oil, 92% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 3H), 7.03 – 6.96 (m, 1H), 4.81 (s, 1H), 4.76 (s, 1H), 3.08 – 2.98 (m, 2H), 2.39 – 2.30 (m, 5H), 1.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 138.8, 136.5, 130.0, 128.9, 126.9, 126.3, 111.6, 37.5, 32.0, 22.5, 21.5. **IR** (ATR): 2916, 1475, 888, 856, 770, 688 cm^{-1}. **HRMS** calculated for $C_{12}H_{16}S$ $[M]^+$ 192.0973, found 192.0970.

(2-fluorophenyl)(3-methylbut-3-en-1-yl)sulfane (6md)



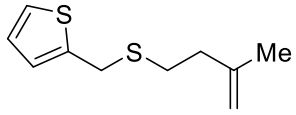
Method A, colorless oil, 91% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.34 (m, 1H), 7.25 – 7.18 (m, 1H), 7.16 – 7.02 (m, 2H), 4.80 (s, 1H), 4.74 (s, 1H), 3.13 – 2.96 (m, 2H), 2.42 – 2.28 (m, 2H), 1.75 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.7 (d, *J* = 245.4 Hz), 143.7, 132.2 (d, *J* = 1.9 Hz), 128.4 (d, *J* = 7.9 Hz), 124.6 (d, *J* = 3.7 Hz), 123.4 (d, *J* = 17.6 Hz), 115.8 (d, *J* = 22.6 Hz), 111.8, 37.5, 31.7 (d, *J* = 2.5 Hz), 22.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.9. **IR** (ATR): 2914, 2360, 1510, 1247, 1174, 1034, 829 cm^{-1}. **HRMS** calculated for $C_{11}H_{13}FSNa$ $[M+Na]^+$ 219.0620, found 219.0618.

2-(((3-methylbut-3-en-1-yl)thio)methyl)furan (6nd)



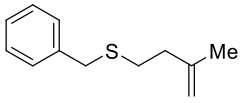
Method B, colorless oil, 64% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.35 (m, 1H), 6.31 (dd, *J* = 3.0, 1.7 Hz, 1H), 6.19 – 6.17 (m, 1H), 4.77 (d, *J* = 0.6 Hz, 1H), 4.74 – 4.70 (m, 1H), 3.74 (s, 2H), 2.65 – 2.59 (m, 2H), 2.30 – 2.23 (m, 2H), 1.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.0, 144.1, 142.2, 111.5, 110.6, 107.5, 37.7, 30.1, 28.5, 22.4. **IR** (ATR): 2919, 1649, 1150, 1010, 886, 735 cm^{-1}. **HRMS** calculated for $C_{10}H_{14}OS$ $[M]^+$ 182.0765, found 182.0757.

2-(((3-methylbut-3-en-1-yl)thio)methyl)thiophene (6od)



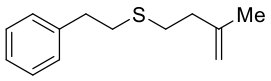
Method B, colorless oil, 65% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 4.9, 1.4 Hz, 1H), 6.95 – 6.88 (m, 2H), 4.77 (s, 1H), 4.71 (s, 1H), 3.94 (s, 2H), 2.61 (dd, *J* = 8.4, 7.1 Hz, 2H), 2.28 (t, *J* = 7.7 Hz, 2H), 1.71 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.1, 142.3, 126.8, 126.2, 125.0, 111.5, 37.6, 30.8, 29.9, 22.4. **IR** (ATR): 2922, 1435, 1035, 889, 850 cm^{-1}. **HRMS** calculated for $C_{10}H_{15}S_2$ $[M+H]^+$ 199.0615, found 199.0623.

benzyl(3-methylbut-3-en-1-yl)sulfane (6pd)



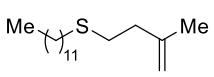
Method B, colorless oil, 90% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.28 – 7.22 (m, 1H), 4.77 (s, 1H), 4.71 (s, 1H), 3.74 (s, 2H), 2.58 – 2.51 (m, 2H), 2.32 – 2.23 (m, 2H), 1.71 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 138.7, 129.0, 128.7, 127.1, 111.4, 37.7, 36.5, 29.7, 22.3. **IR** (ATR): 2923, 2360, 1057, 970, 794 cm^{-1}. **HRMS** calculated for $C_{12}H_{17}S$ $[M+H]^+$ 193.1051, found 193.0942.

(3-methylbut-3-en-1-yl)(phenethyl)sulfane (6qd)



Method B, colorless oil, 54% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 5H), 4.85 (s, 1H), 4.81 (s, 1H), 3.01 – 2.93 (m, 2H), 2.92 – 2.83 (m, 2H), 2.77 – 2.66 (m, 2H), 2.42 – 2.32 (m, 2H), 1.82 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.3, 140.8, 128.7, 126.5, 111.4, 38.0, 36.6, 33.9, 30.7, 22.4. **IR** (ATR): 2923, 1496, 1453, 1030, 747 cm^{-1}. **HRMS** calculated for $C_{13}H_{19}S$ $[M+H]^+$ 207.1207, found 207.1205.

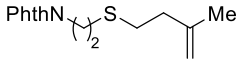
dodecyl(3-methylbut-3-en-1-yl)sulfane (6rd)



Method B, colorless oil, 55% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.77 (s, 1H), 4.73 (s, 1H), 2.67 – 2.59 (m, 2H), 2.57 – 2.49 (m, 2H), 2.33 – 2.25 (m, 2H), 1.74 (s, 3H), 1.63 – 1.50 (m, 3H), 1.41 – 1.19 (m, 17H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 111.3, 38.1, 32.4, 32.1, 30.5, 29.9, 29.84,

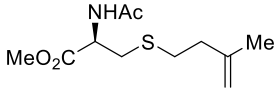
29.82, 29.79, 29.72, 29.5, 29.4, 29.1, 22.9, 22.4, 14.3. **IR** (ATR): 2922, 2852, 2360, 1457, 888, 721 cm^{-1}. **HRMS** calculated for $C_{17}H_{35}S$ $[M+H]^+$ 271.2459, found 271.2446.

3-(2-((3-methylbut-3-en-1-yl)thio)ethyl)isoindoline (6sd)



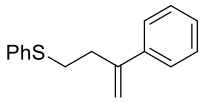
Method B, colorless oil, 62% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.76 – 7.68 (m, 2H), 4.77 (s, 1H), 4.74 (s, 1H), 3.93 – 3.85 (m, 2H), 2.88 – 2.78 (m, 2H), 2.71 (dd, *J* = 8.3, 7.1 Hz, 2H), 2.30 (t, *J* = 7.7 Hz, 2H), 1.74 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.3, 144.0, 134.2, 132.2, 123.5, 111.6, 37.8, 37.3, 30.2, 30.0, 22.3. **IR** (ATR): 2925, 1709, 1392, 1356, 1085, 714 cm^{-1}. **HRMS** calculated for $C_{15}H_{18}NS$ $[M+H]^+$ 276.1058, found 276.1067.

methyl *N*-acetyl-*S*-(3-methylbut-3-en-1-yl)-*L*-cysteinate (6bd)



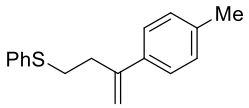
Method B, white solid, 63% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.30 (d, *J* = 6.4 Hz, 1H), 4.83 (dt, *J* = 7.7, 5.0 Hz, 1H), 4.77 (s, 1H), 4.71 (s, 1H), 3.77 (s, 3H), 3.06 – 2.93 (m, 2H), 2.65 – 2.58 (m, 2H), 2.26 (t, *J* = 7.7 Hz, 2H), 2.04 (s, 3H), 1.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.6, 170.0, 143.7, 111.7, 52.8, 52.1, 37.8, 34.4, 31.0, 23.3, 22.3. **IR** (ATR): 3274, 1744, 1538, 1436, 1211, 1175 cm^{-1}. **HRMS** calculated for $C_{11}H_{20}NO_3S$ $[M+H]^+$ 246.1164, found 246.1164.

phenyl(3-phenylbut-3-en-1-yl)sulfane (6ae)



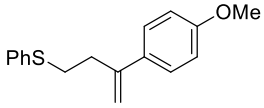
Method A, colorless oil, 82% yield, 15:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 9H), 7.22 –7.14 (m, 1H), 5.35 (s, 1H), 5.13 (s, 1H), 3.06 – 2.97 (m, 2H), 2.84 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.8, 140.5, 136.5, 129.6, 129.1, 128.6, 127.8, 126.3, 126.2, 113.9, 35.5, 32.7. **IR** (ATR): 2360, 1480, 1438, 898, 777, 737, 690 cm^{-1}. **HRMS** calculated for $C_{16}H_{16}S$ $[M]^+$ 240.0973, found 240.0979.

phenyl(3-(*p*-tolyl)but-3-en-1-yl)sulfane (6af)



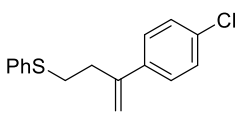
Method A, colorless oil, 88% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 6H), 7.22 – 7.13 (m, 3H), 5.33 (d, *J* = 1.0 Hz, 1H), 5.09 (d, *J* = 1.0 Hz, 1H), 3.06 – 2.99 (m, 2H), 2.87 – 2.79 (m, 2H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.5, 137.6, 137.5, 136.6, 129.5, 129.3, 129.0, 126.2, 126.1, 113.1, 35.5, 32.7, 21.3. **IR** (ATR): 2920, 2360, 1480, 1438, 1025, 823, 736 cm^{-1}. **HRMS** calculated for $C_{17}H_{18}S$ $[M]^+$ 254.1129, found 254.1136.

(3-(4-methoxyphenyl)but-3-en-1-yl)(phenyl)sulfane (6ag)



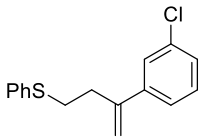
Method A, colorless oil, 74% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 6H), 7.27 – 7.23 (m, 1H), 6.95 – 6.90 (m, 2H), 5.34 (d, *J* = 1.2 Hz, 1H), 5.10 (d, *J* = 1.2 Hz, 1H), 3.88 (s, 3H), 3.12 – 3.04 (m, 2H), 2.92 – 2.84 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.4, 146.0, 136.6, 132.8, 129.5, 129.1, 127.4, 126.1, 114.0, 112.3, 55.5, 35.5, 32.7. **IR** (ATR): 2957, 1605, 1512, 1249, 1184, 1028, 889, 730 cm^{-1}. **HRMS** calculated for $C_{17}H_{18}OS$ $[M]^+$ 270.1078, found 270.1078.

(3-(4-chlorophenyl)but-3-en-1-yl)(phenyl)sulfane (6ah)



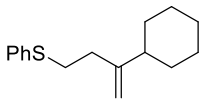
Method A, colorless oil, 95% yield, 13:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.16 (m, 9H), 5.33 (s, 1H), 5.14 (s, 1H), 3.03 – 2.96 (m, 2H), 2.81 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 138.9, 136.3, 133.6, 129.7, 129.1, 128.7, 127.6, 126.3, 114.5, 35.3, 32.6. **IR** (ATR): 2922, 1491, 1438, 1091, 1011, 902, 833, 736 cm^{-1}. **HRMS** calculated for $C_{16}H_{15}ClS$ $[M]^+$ 274.0583, found 274.0597.

(3-(3-chlorophenyl)but-3-en-1-yl)(phenyl)sulfane (6ai)



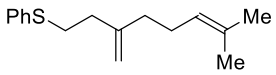
Method A, colorless oil, 86% yield, 8:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.12 (m, 9H), 5.36 (s, 1H), 5.17 (s, 1H), 3.10 – 2.91 (m, 2H), 2.80 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.6, 142.4, 136.2, 134.6, 129.8, 129.7, 129.1, 127.8, 126.5, 126.3, 124.5, 115.1, 35.3, 32.6. **IR** (ATR): 2917, 1560, 1478, 901, 883, 789, 736 cm^{-1}. **HRMS** calculated for $C_{16}H_{15}ClS$ $[M]^+$ 274.0583, found 274.0574.

(4-cyclohexylbut-3-en-1-yl)(phenyl)sulfane (6aj)



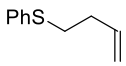
Method A, colorless oil, 60% yield, >20:1 *rr*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.21 – 7.15 (m, 1H), 4.82 (s, 1H), 4.76 (d, *J* = 1.3 Hz, 1H), 3.06 – 2.99 (m, 2H), 2.42 – 2.33 (m, 2H), 1.93 – 1.60 (m, 7H), 1.34 – 1.08 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.6, 137.0, 129.2, 129.1, 126.0, 108.5, 44.4, 34.7, 32.7, 32.6, 26.9, 26.5. **IR** (ATR): 2923, 2850, 1480, 1438, 1025, 887, 735 cm^{-1}. **HRMS** calculated for $C_{16}H_{23}S$ $[M+H]^+$ 247.1521, found 247.1529.

(5-methyl-3-methyleneoct-6-en-1-yl)(phenyl)sulfane (6aa)



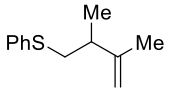
Method A, colorless oil, 60% yield, >20:1 *rr*. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 5.16 (t, *J* = 6.0 Hz, 1H), 4.89 (s, 1H), 4.87 (s, 1H), 3.14 – 3.04 (m, 2H), 2.43 (t, *J* = 7.8 Hz, 2H), 2.21 – 2.05 (m, 4H), 1.75 (s, 3H), 1.66 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.8, 136.8, 132.0, 129.3, 129.1, 126.0, 124.0, 110.6, 36.1, 35.9, 32.3, 26.6, 25.9, 17.9. **IR** (ATR): 2924, 2360, 1438, 1025, 891, 736 cm^{-1}. **HRMS** calculated for $C_{16}H_{23}S$ $[M+H]^+$ 247.1521, found 247.1522.

but-3-en-1-yl(phenyl)sulfane (6ak)[8]



Method A, colorless oil, 28% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 4H), 7.23 (d, *J* = 5.9 Hz, 1H), 5.98 – 5.85 (m, 1H), 5.20 – 5.06 (m, 2H), 3.08 – 2.97 (m, 2H), 2.51 – 2.39 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.6, 136.6, 129.5, 129.1, 126.1, 116.4, 33.5, 33.2. **IR** (ATR): 2967, 1584, 1480, 1438, 1091, 1025, 993, 915, 736 cm^{-1}. **HRMS** calculated for $C_{10}H_{12}S$ $[M]^+$ 164.0660, found 164.0664.

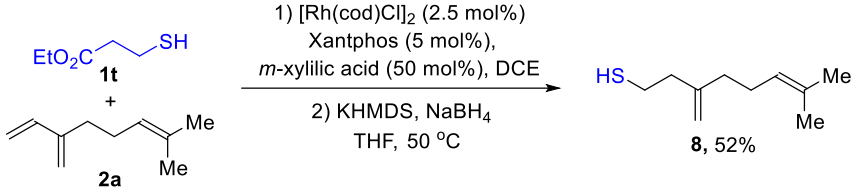
(2,3-dimethylbut-3-en-1-yl)(phenyl)sulfane (6al)



Method A, colorless oil, 73% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.26 – 7.20 (m, 1H), 4.91 – 4.81 (m, 2H), 3.11 (dd, *J* = 12.5, 6.7 Hz, 1H), 2.91 (dd, *J* = 12.5, 7.6 Hz, 1H), 2.58 – 2.46 (m, 1H), 1.78 (d, *J* = 0.7 Hz, 3H), 1.23 (d, *J* = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.4, 137.3, 129.2, 129.0,

125.9, 111.0, 40.7, 39.4, 19.5, 19.2. **IR** (ATR): 2965, 1645, 1584, 1480, 1438, 1374, 890, 735, 689 cm^{-1}. **HRMS** calculated for $C_{12}H_{16}S$ $[M]^+$ 192.0973, found 192.0980.

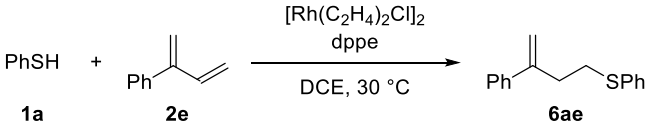
Synthesis of compound 8



In a N_2-filled glovebox, Xantphos (4.6 mg, 0.008 mmol) and DCE (0.60 mL) were added to a 1-dram vial containing $[Rh(cod)Cl]_2$ (2.0 mg, 0.004 mmol). The resulting mixture was stirred for 10 min, and then 3,5-dimethylbenzoic acid (12 mg, 0.08 mmol), myrcene (**2a**, 43.6 mg, 0.32 mmol) and thiol **1t** (21.5 mg, 0.16 mmol) were added. The mixture was held at 30 °C until no starting material was observed by TLC. DCE was removed under reduced pressure. The residual oil was dissolved in THF (1.5 mL), followed by adding KHMDS (95.8 mg, 0.48 mmol) and $NaBH_4$ (1.2 mg, 0.032 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 12 h at 50 °C. After cooled to 0 °C, 1M HCl was added to quench the reaction. The residue was extracted with EtOAc and the resulting organic layer was washed with saturated brine. The combined organic layer was concentrated and then purified by flash column chromatography on silica gel (hexane) to yield the desired product **8** as a colorless oil (14.2 mg, 52% yield, >20:1 *rr*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.10 (t, *J* = 6.4 Hz, 1H), 4.84 (s, 1H), 4.79 (s, 1H), 2.69 – 2.58 (m, 2H), 2.34 (t, *J* = 7.3 Hz, 2H), 2.18 – 2.08 (m, 2H), 2.06 – 1.97 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.43 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.2, 132.1, 124.0, 111.2, 40.6, 35.9, 26.5, 25.9, 23.0, 17.9. **IR** (ATR): 2924, 1737, 1446, 1375, 1228, 1007 cm^{-1}. **HRMS** calculated for $C_{10}H_{18}S$ $[M]^+$ 170.1129, found 170.1123.

6. Mechanism studies for 3,4-*anti*-Markovnikov hydrothiolation

6.1 Kinetic studies:



The kinetic profile of the reaction was studied by obtaining initial rates with different concentrations of thiophenol (**1a)**, 1,3-diene **2e**, and Rh-catalyst. No products of decomposition are observed for the system. The rates were monitored by GC-FID analysis using 1,3,5-trimethoxybenzene as an internal standard.

Determination of the reaction order in catalyst

Representative procedure (entry 1):

In a N_2-filled glove box, a 0.0125M catalyst solution was prepared by combining $[Rh(C_2H_4)_2Cl]_2$ (2.4 mg, 0.00625 mmol), dppe (5.0 mg, 0.0125 mmol), and DCE (1.0 mL). A solution of reagents was prepared by combining **1a** (55.1 mg, 0.50 mmol), **2e** (97.7 mg, 0.750 mmol), and DCE (1.0 mL). A vial was charged with a stir bar and 1,3,5-trimethoxybenzene (6.0 mg, 0.036 mmol). Catalyst solution (80 µL) was added to the vial, followed by 0.2 mL of reagent solution. Additional DCE

was added to the vial to make a total reaction volume of 0.4 mL, and the vial was sealed with a Teflon cap. Aliquots (10 µL) were taken every 5 minutes and quenched in 2 mL of EtOAc. The reaction halts in EtOAc. The amount of **6ae** was monitored by GC-FID analysis.

Table S5. Observed rate versus catalyst concentration for 3,4-*anti*-Markovnikov hydrothiolation

entry	1	2	3	4
[Rh] (M)	0.0025	0.00375	0.005	0.00625
k_{obs} (M/min)	5.74×10^{-4}	8.14×10^{-4}	9.98×10^{-4}	14.0×10^{-4}

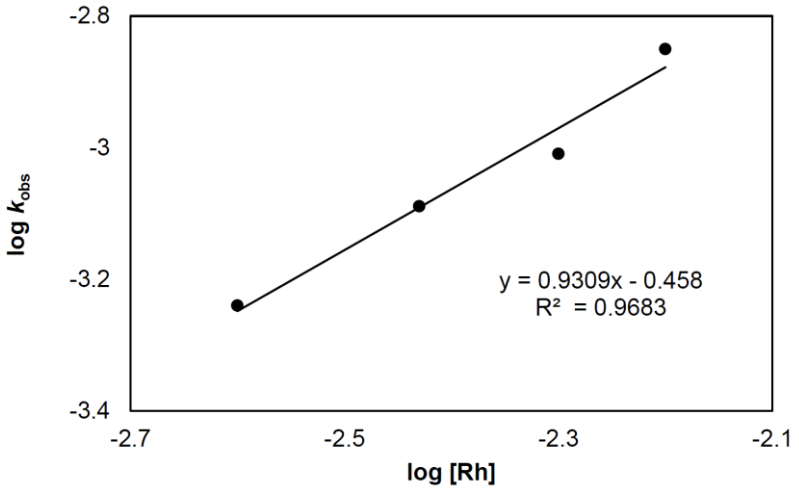


Figure S14. Plot of logk_{obs} vs log[Rh] for 3,4-*anti*-Markovnikov hydrothiolation (first order)

Determination of the reaction order in diene 2e

Representative procedure (entry 1):

In a N_2-filled glove box, a 0.005M catalyst solution was prepared by combining $[Rh(C_2H_4)_2Cl]_2$ (1.9 mg, 0.005 mmol), dppe (4.0 mg, 0.01 mmol), and DCE (2.0 mL). A solution of **1a** (110.2 mg, 1.0 mmol) in DCE (2.0 mL) was prepared. A vial was charged with a stir bar, 1,3,5-trimethoxybenzene (6.0 mg, 0.036 mmol), and **2e** (13.0 mg, 0.1 mmol). Catalyst solution (0.2 mL) was added to the vial, followed by 0.2 mL of **1a** solution, and the vial was sealed with a Teflon cap. Aliquots (10 µL) were taken every 5 minutes and quenched in 2 mL of EtOAc. The reaction halts in EtOAc. The amount of **6ae** was monitored by GC-FID analysis.

Table S6. Observed rate versus 1,3-diene **2e** concentration for 3,4-*anti*-Markovnikov hydrothiolation

entry	1	2	3	4	5
[**2e**] (Initial) (M)	0.25	0.5	0.75	1.0	1.25
k_{obs} (M/min)	1.82×10^{-4}	3.67×10^{-4}	5.88×10^{-4}	7.58×10^{-4}	8.93×10^{-4}

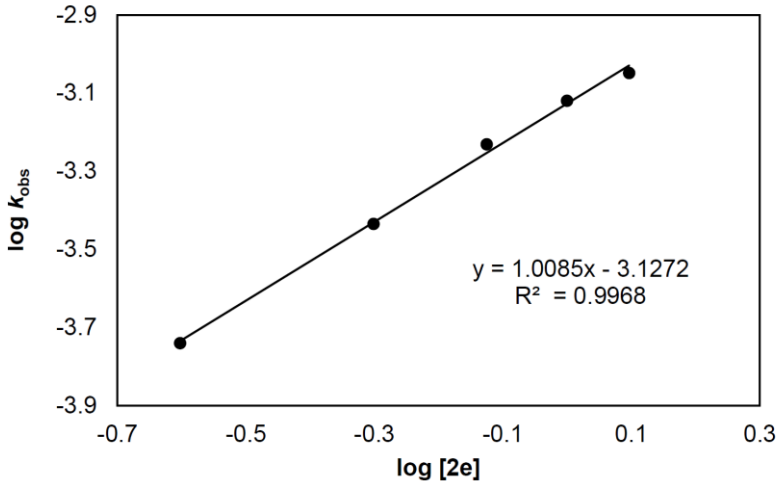


Figure S15. Plot of logk_{obs} vs log[**2e**] for 3,4-*anti*-Markovnikov hydrothiolation (first order)

Determination of the reaction order in thiophenol (1a)

Representative procedure (entry 1):

In a N_2-filled glove box, a 0.005M catalyst solution was prepared by combining $[Rh(C_2H_4)_2Cl]_2$ (1.9 mg, 0.005 mmol), dppe (4.0 mg, 0.01 mmol), and DCE (2.0 mL). A solution of **2e** (130.2 mg, 1.0 mmol) in DCE (2.0 mL) was prepared. A vial was charged with a stir bar, 1,3,5-trimethoxybenzene (6.0 mg, 0.036 mmol), and **1a** (6.0 mg, 0.05 mmol). Catalyst solution (0.2 mL) was added to the vial, followed by 0.2 mL of **2e** solution, and the vial was sealed with a Teflon cap. Aliquots (10 µL) were taken every 5 minutes and quenched in 2 mL of EtOAc. The reaction halts in EtOAc. The amount of **6ae** was monitored by GC-FID analysis.

Table S7. Observed rate versus thiophenol **1a** concentration for 3,4-*anti*-Markovnikov hydrothiolation

entry	1	2	3	4	5
[**1a**] (Initial) (M)	0.125	0.25	0.375	0.5	0.625
k_{obs} (M/min)	5.81×10^{-4}	4.57×10^{-4}	3.47×10^{-4}	2.86×10^{-4}	2.45×10^{-4}

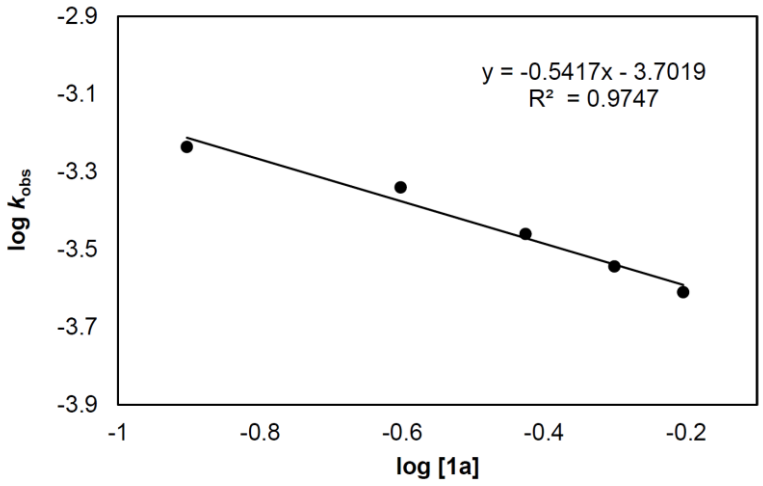
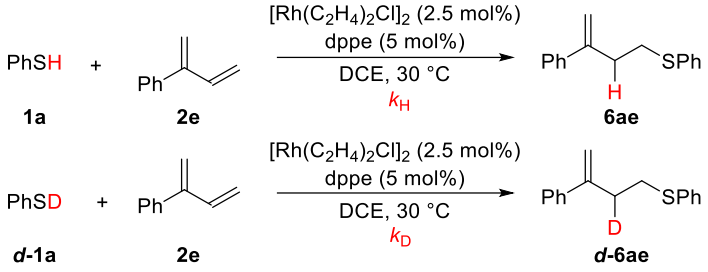
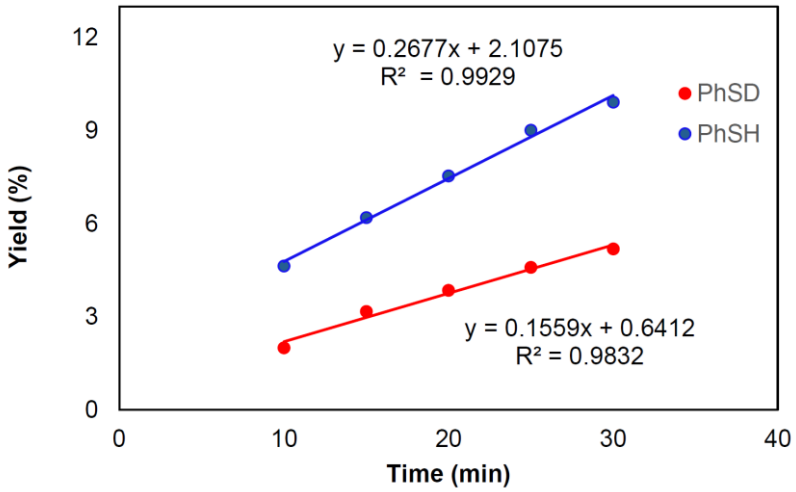


Figure S16. Plot of logk_{obs} vs log[**1a**] for 3,4-*anti*-Markovnikov hydrothiolation (-0.5 order)

6.2 Initial rate *KIE* study

In a N_2-filled glove box, a 0.005M catalyst solution was prepared by combining $[Rh(C_2H_4)_2Cl]_2$ (1.0 mg, 0.0025 mmol), dppe (2.0 mg, 0.005 mmol), and DCE (1.0 mL). A solution of **2e** (65.1 mg, 0.5 mmol) in DCE (1.0 mL) was prepared. A vial was charged with a stir bar, 1,3,5-trimethoxybenzene (6.0 mg, 0.036 mmol), and **1a** (11.0 mg, 0.1 mmol) or ***d*-1a** (11.1 mg, 0.1 mmol). Catalyst solution (0.2 mL) was added to the vial, followed by 0.2 mL of **2e** solution, and the vial was sealed with a Teflon cap. Aliquots (10 µL) were taken every 5 minutes and quenched in 2 mL of EtOAc. The reaction halts in EtOAc. The amount of **6ae** was monitored by GC-FID analysis.





adjusted initial rate of deutro species (considering 14% PhSH):

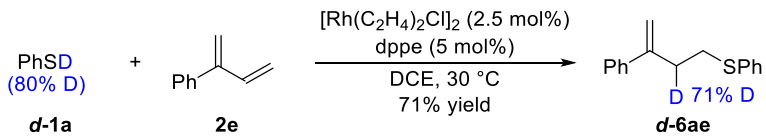
$$0.156 = 0.86\ k_D + 0.14 \times 0.268$$

$$k_D = 0.138$$

Calculation of KIE: $k_H/k_D = 0.268/0.138 = 1.9$

Figure S17. Initial rate *KIE* for 3,4-*anti*-Markovnikov hydrothiolation

6.3 Deuterium-labeling study



In a N_2-filled glovebox, dppe (2.0 mg, 0.005 mmol) and DCE (0.40 mL) were added to a 1-dram vial containing $[Rh(C_2H_4)_2Cl]_2$ (1.0 mg, 0.0025 mmol). The resulting mixture was stirred for

10 min, and then 1,3-diene **2e** (19.5 mg, 0.15 mmol) and thiol ***d*-1a** (11.1 mg, 0.10 mmol) were added. The mixture was held at 30 °C until no starting material was observed by TLC. The resulting mixture was then cooled to rt. The product ***d*-6ae** (17.1 mg, 71% yield) was purified by preparative thinlayer chromatography (hexanes/ EtOAc = 40/1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 9H), 7.21 – 7.16 (m, 1H), 5.34 (s, 1H), 5.12 (s, 1H), 3.04 – 2.97 (m, 2H), 2.85 – 2.80 (m, 1.29H).

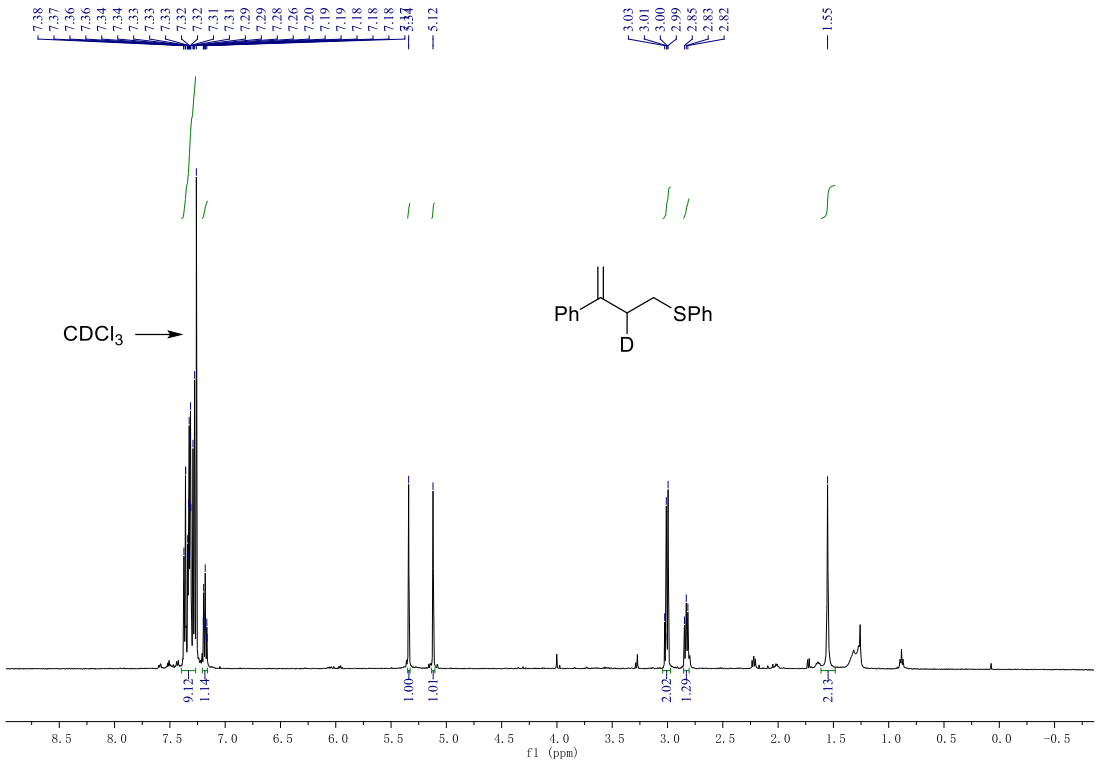


Figure S18. ^{1}H NMR [500 MHz, $CDCl_3$ (δ 7.26 ppm)] for ***d*-6ae**

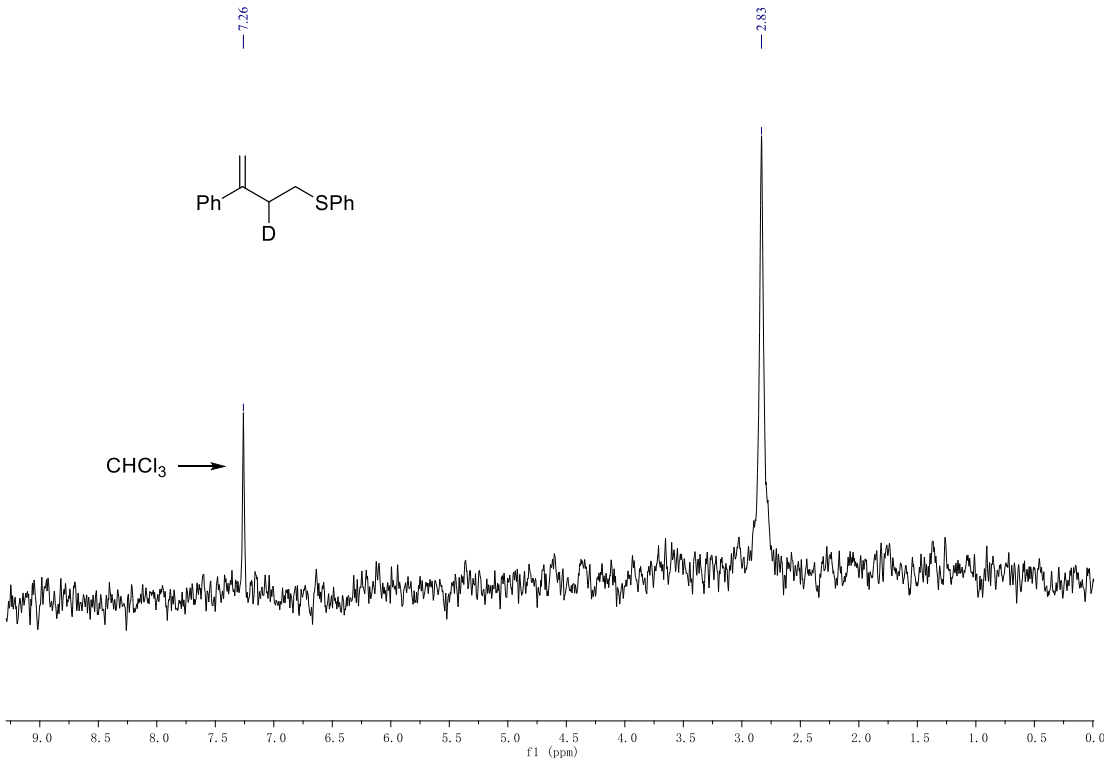


Figure S19. ^{2}H NMR [500 MHz, $CHCl_3$ (δ 7.26 ppm)] for ***d*-6ae**

6.4 NMR studies

In a N_2-filled glovebox, dppe (8.0 mg, 0.02 mmol) and DCE-d_4 (0.80 mL) were added to a 1-dram vial containing $[Rh(C_2H_4)_2Cl]_2$ (3.9 mg, 0.01 mmol). The resulting mixture was stirred for 10 min and then thiophenol (**1a**, 22.0 mg, 0.20 mmol) was added. The reaction mixture was transferred to a J. Young NMR tube to perform ^{1}H NMR and ^{31}P NMR spectroscopy. A resonance at −15.8 ppm was observed in less than ten minutes at rt in the ^{1}H NMR spectrum (Figure S20) and an equivalent phosphine resonance in the ^{31}P NMR spectrum [doublet (δ = 52.2 ppm, $J_{Rh–P}$ = 94 Hz)] was observed (Figure S21). The 1,3-diene **2e** (26.0 mg, 0.20 mmol) was then added to this mixture, and we observed the same Rh–H resonance and equivalent resonances in the ^{31}P NMR spectrum during the whole reaction progress. Based on these studies and the kinetic study, we labeled the intermediate **III′** as the resting state for 3,4-*anti*-Markovnikov hydrothiolation.

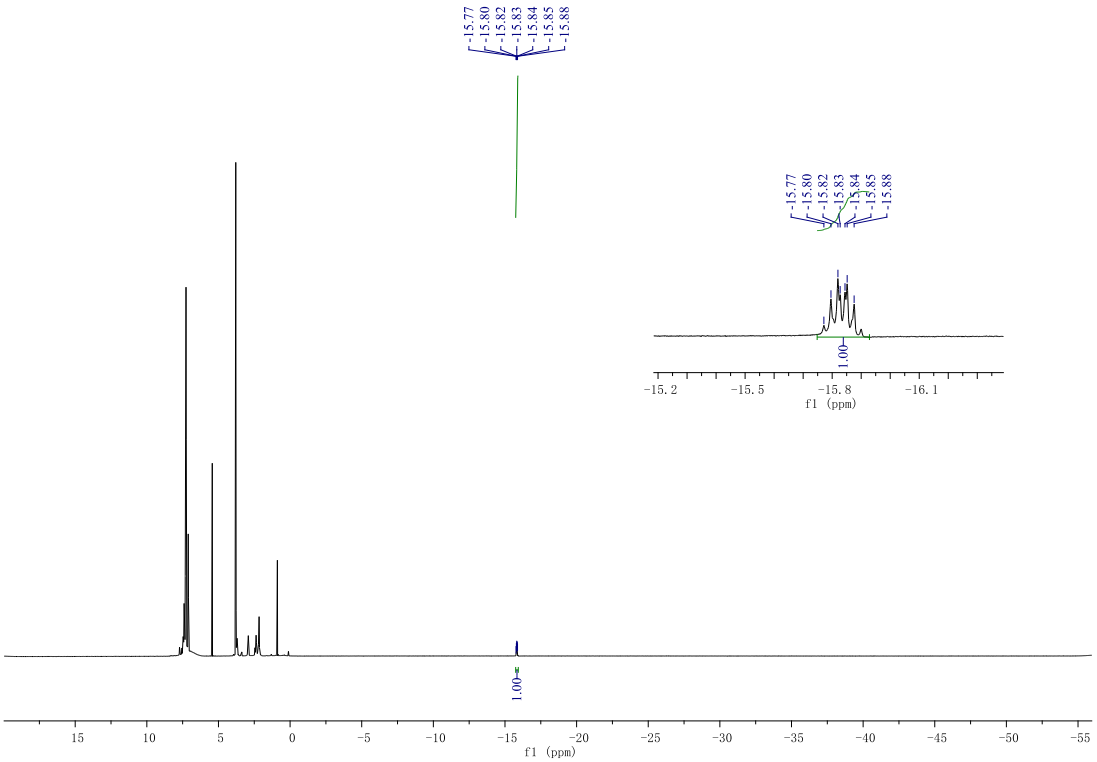


Figure S20. ^{1}H NMR (500 MHz) spectrum for a mixture of [Rh(dppe)Cl]$_2$ and thiolphenol (**1a**) in DCE-d_4 (δ 3.79 ppm)

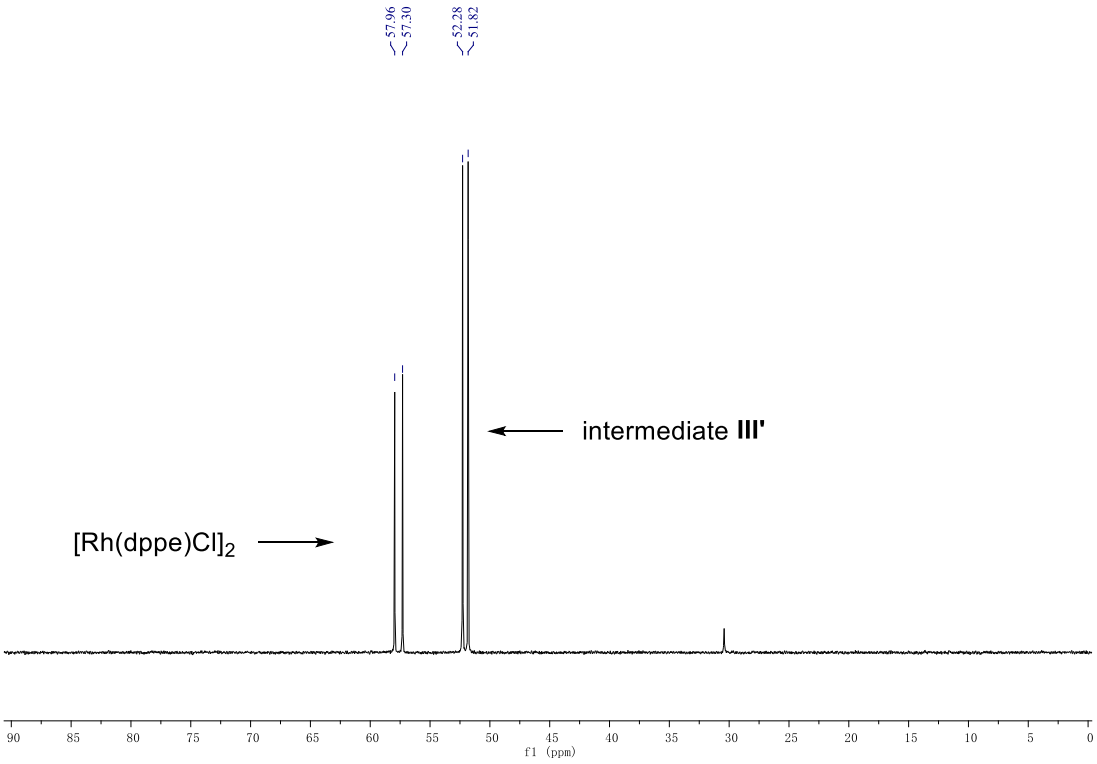


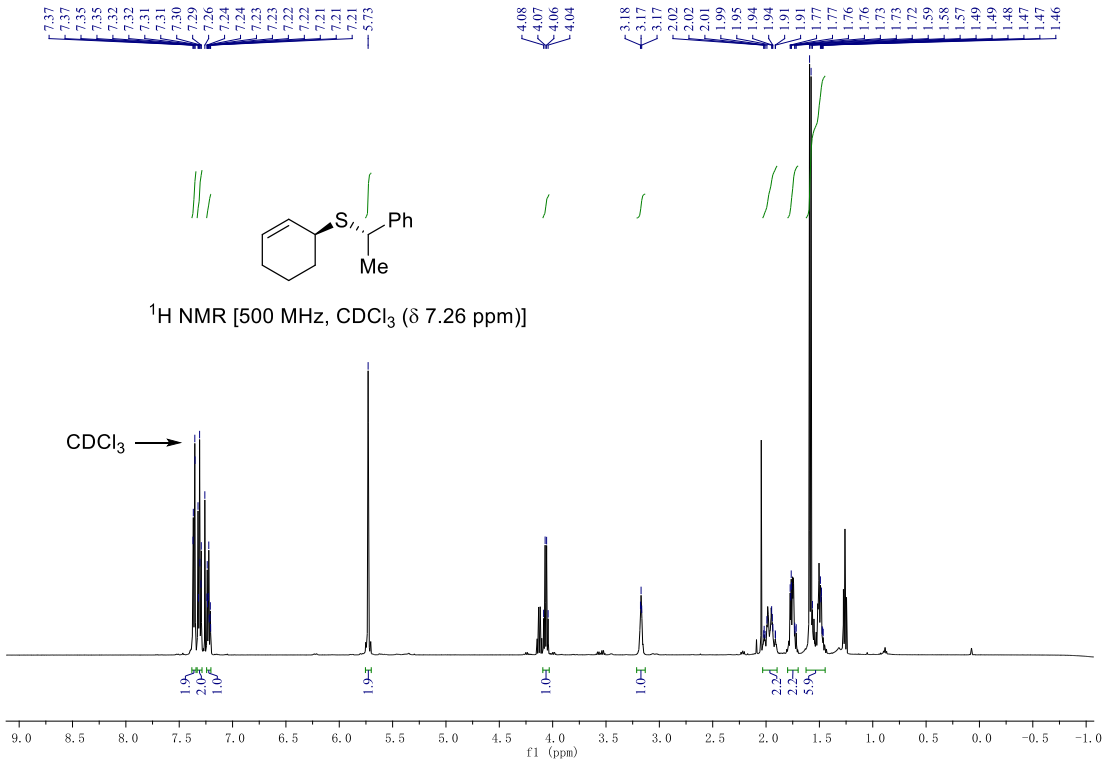
Figure S21. ^{31}P NMR (202 MHz) spectrum for a mixture of [Rh(dppe)Cl]$_2$ and thiolphenol (**1a**) in DCE-d_4

7. References

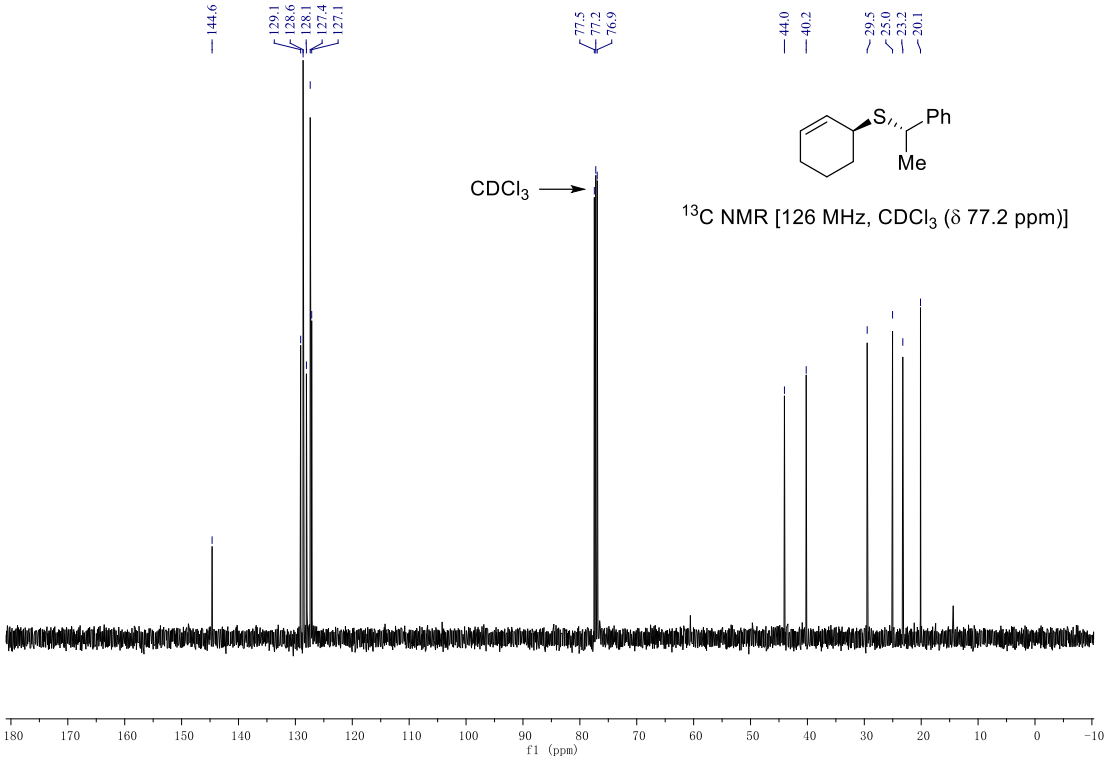
1. Fustero, S.; Bello, P.; Miró, J.; Simón, A.; del Pozo, C. *Chem. Eur. J.* **2012**, *18*, 10991.
2. Kennemur, J. L.; Kortman, G. D.; Hull, K. L. *J. Am. Chem. Soc.* **2016**, *138*, 11914.
3. Jeyakumar, K.; Chakravarthy, D. R.; Chand, D. K. *Catal. Commun.* **2009**, *10*, 1948.
4. Ichikawa, Y.; Kashiwagi, T.; Urano, N. *J. Chem. Soc., Perkin Trans. 1*, **1992**, 1497.
5. Nakamura, H.; Wu, H.; Kobayashi, J.; Ohizumi, Y. *Tetrahedron Lett.* **1983**, *24*, 4105.
6. Cohen, T.; Kreethadumrongdat, T.; Liu, X.; Kulkarni, V. *J. Am. Chem. Soc.* **2001**, *123*, 3478.
7. Shigehisa, H.; Ano, T.; Honma, H.; Ebisawa, K.; Hiroya, K. *Org. Lett.* **2016**, *18*, 3622.
8. Coulter, M. M.; Kou, K. G. M.; Galligan, B.; Dong, V. M. *J. Am. Chem. Soc.* **2010**, *132*, 16330.

8. NMR spectra of unknown compounds

((*S*)-cyclohex-2-en-1-yl)((*S*)-1-phenylethyl)sulfane ((*S*,*S*)-3cb)

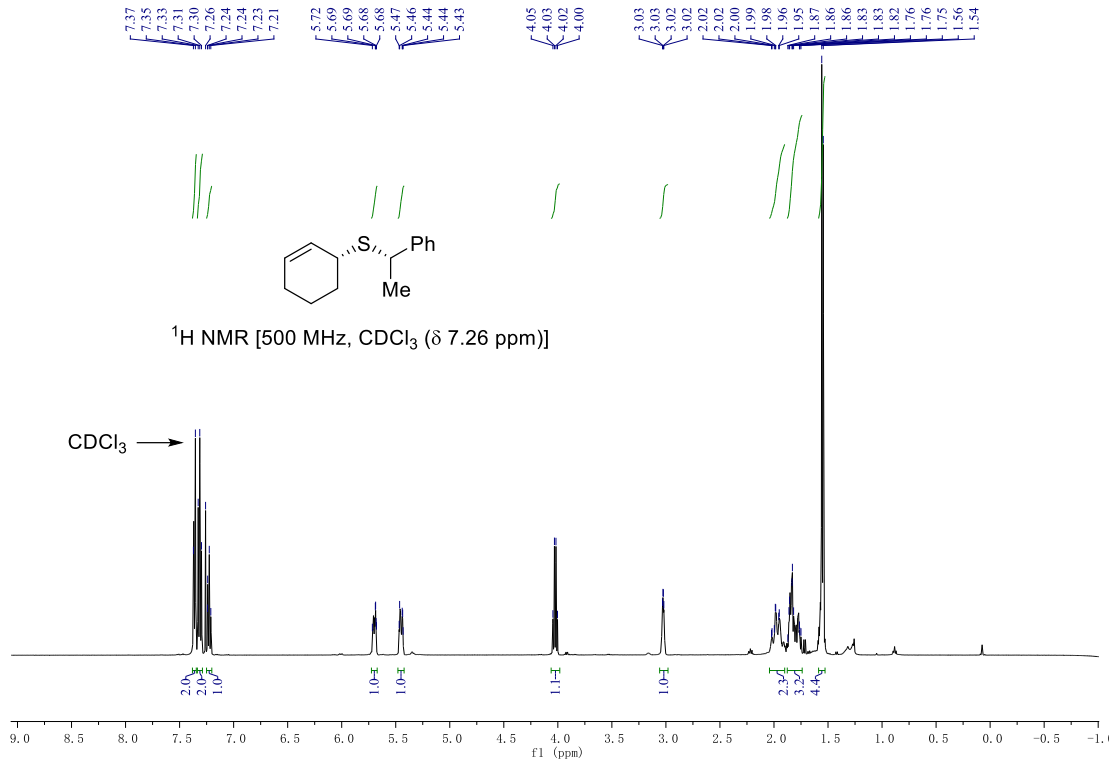


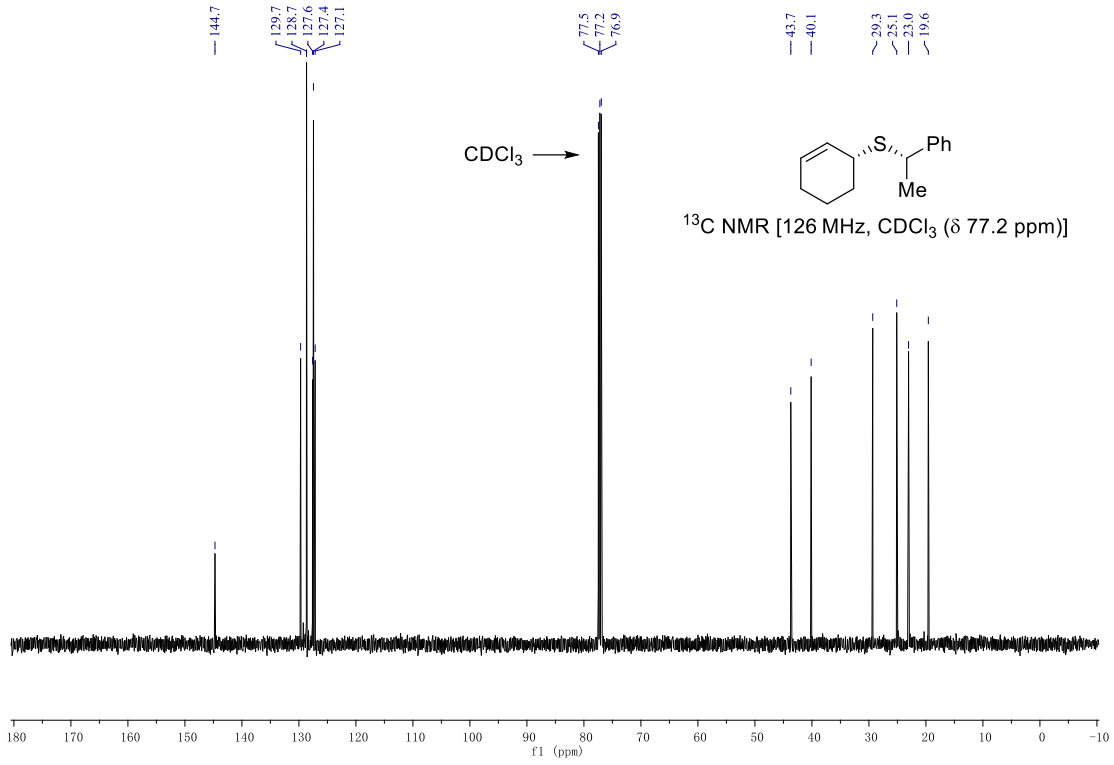
^{1}H NMR [500 MHz, $CDCl_3$ (δ 7.26 ppm)]



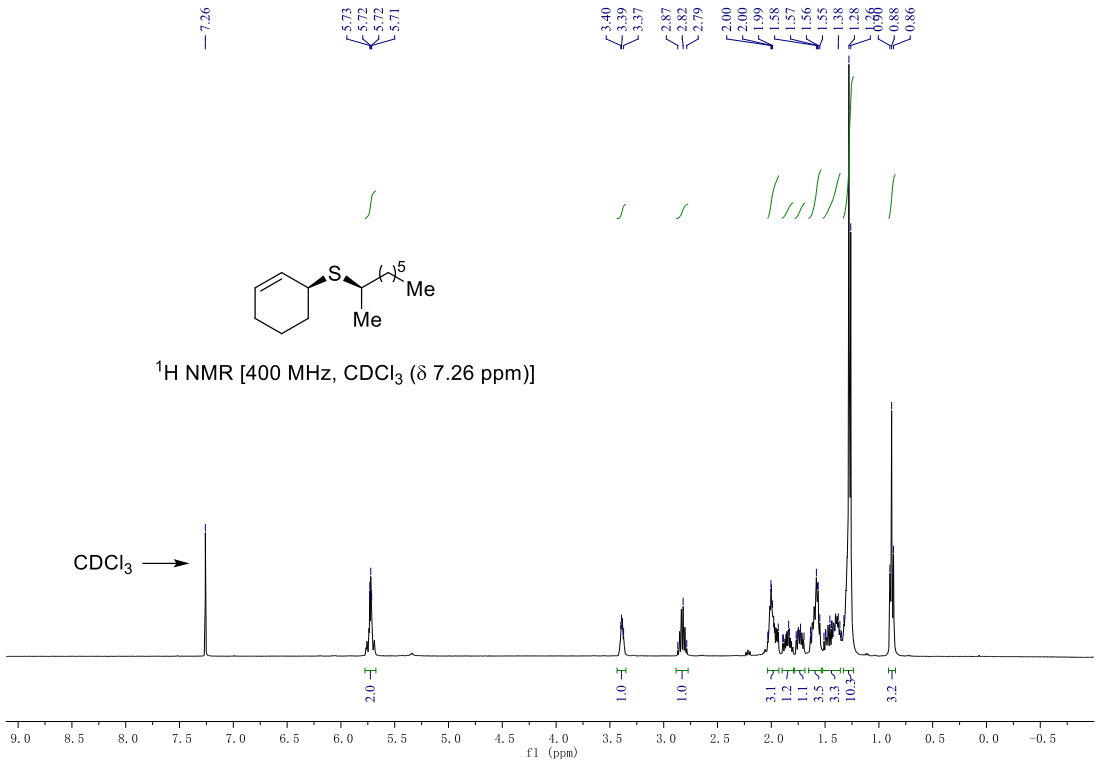
^{13}C NMR [126 MHz, $CDCl_3$ (δ 77.2 ppm)]

((*R*)-cyclohex-2-en-1-yl)((*S*)-1-phenylethyl)sulfane ((*R*,*S*)-3cb)

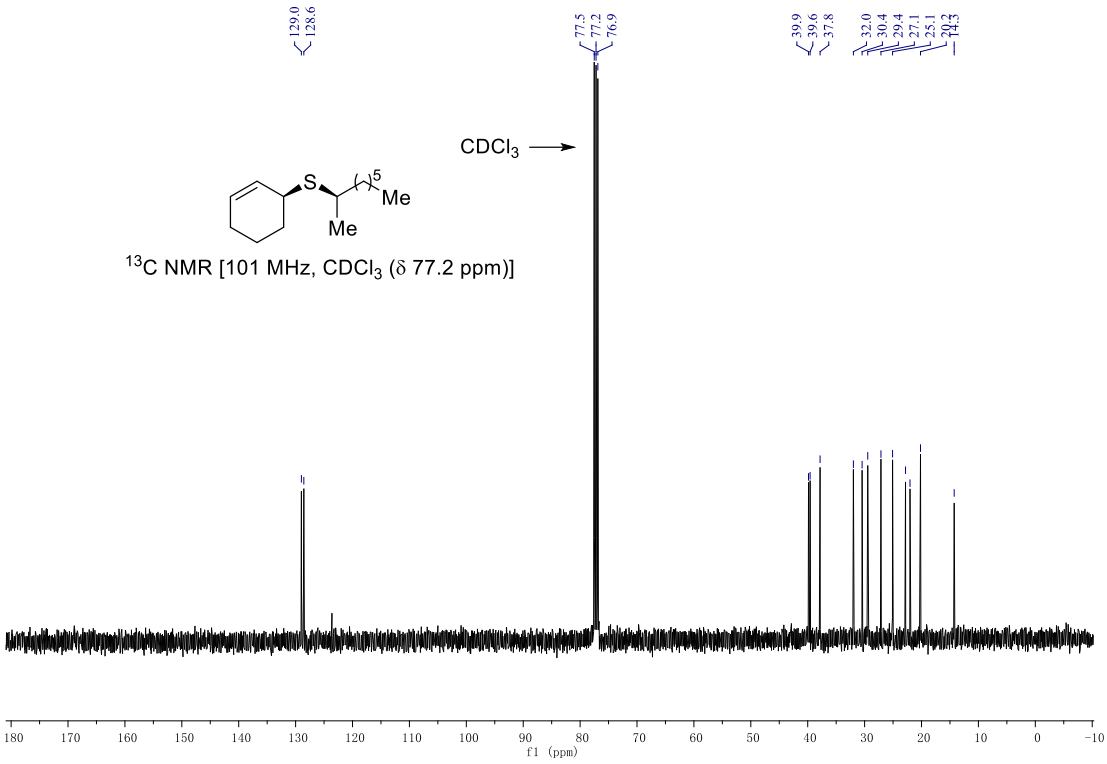




((*S*)-cyclohex-2-en-1-yl)((*R*)-octan-2-yl)sulfane ((*S*,*R*)-3db)

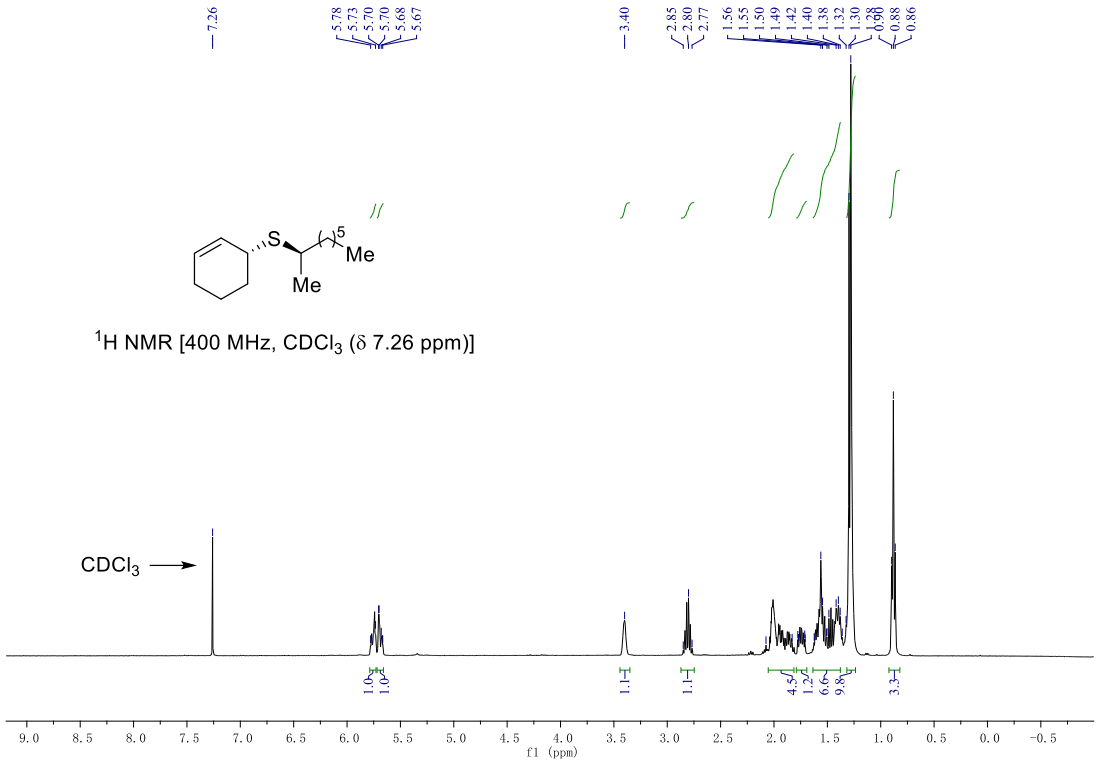


^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)]

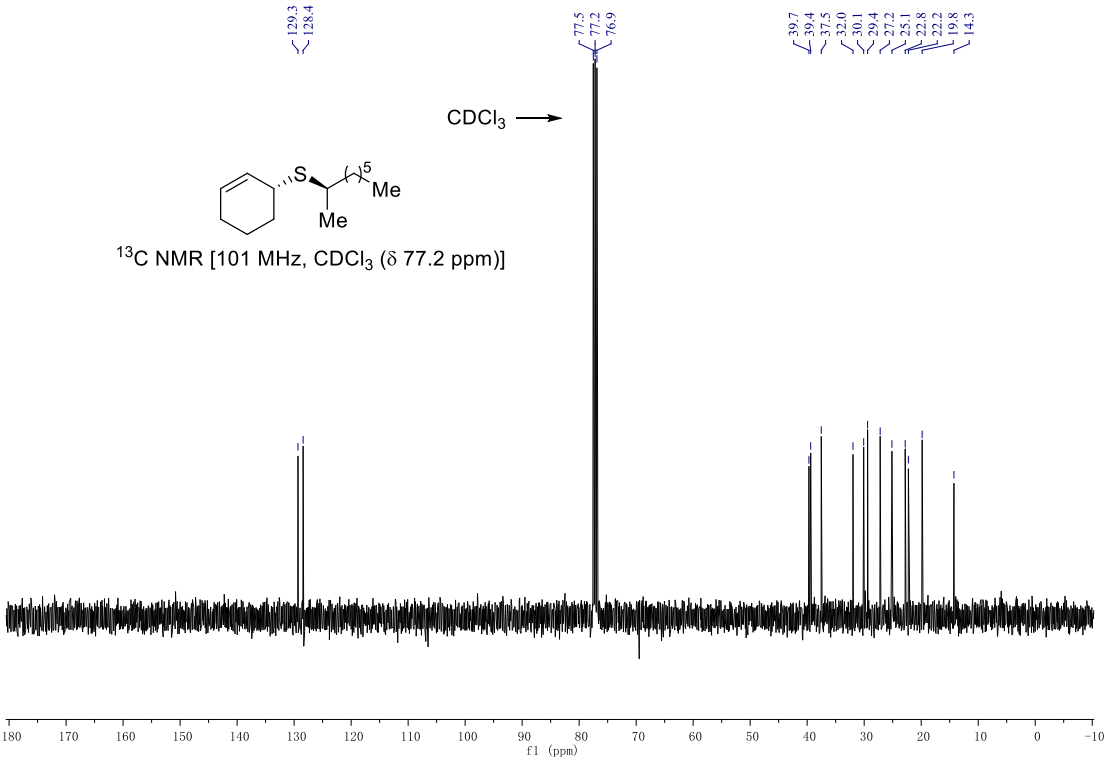


^{13}C NMR [101 MHz, $CDCl_3$ (δ 77.2 ppm)]

((*R*)-cyclohex-2-en-1-yl)((*R*)-octan-2-yl)sulfane ((*R*,*R*)-3db)

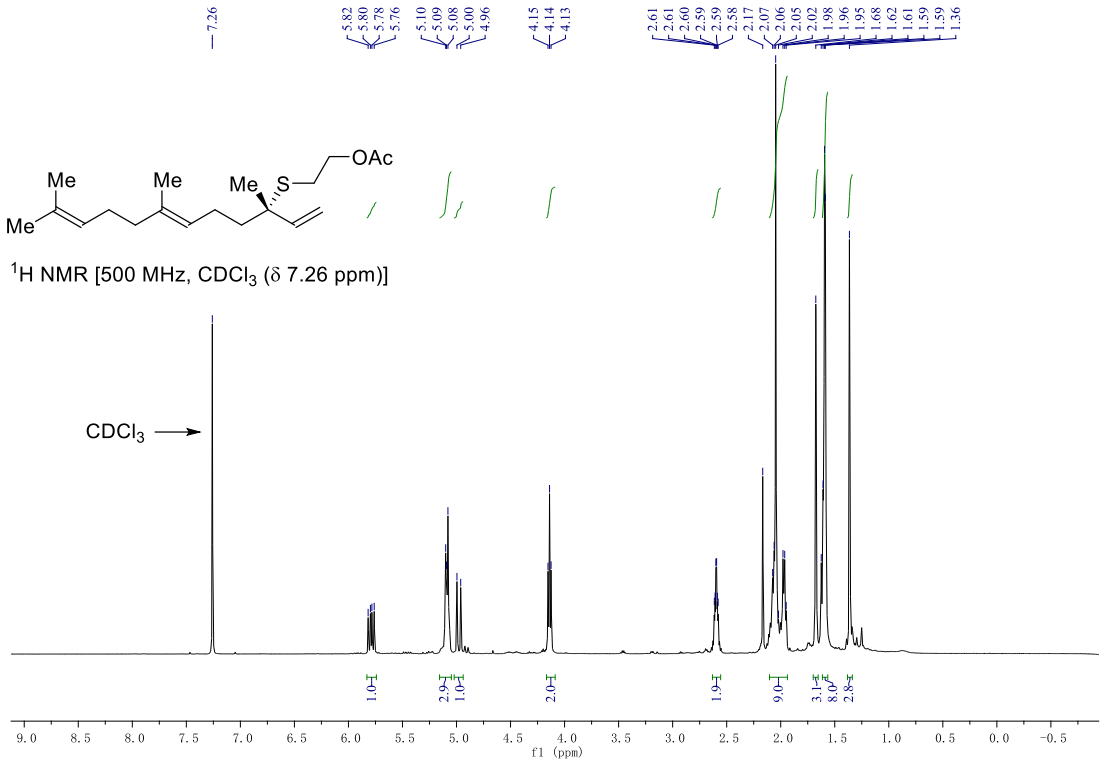


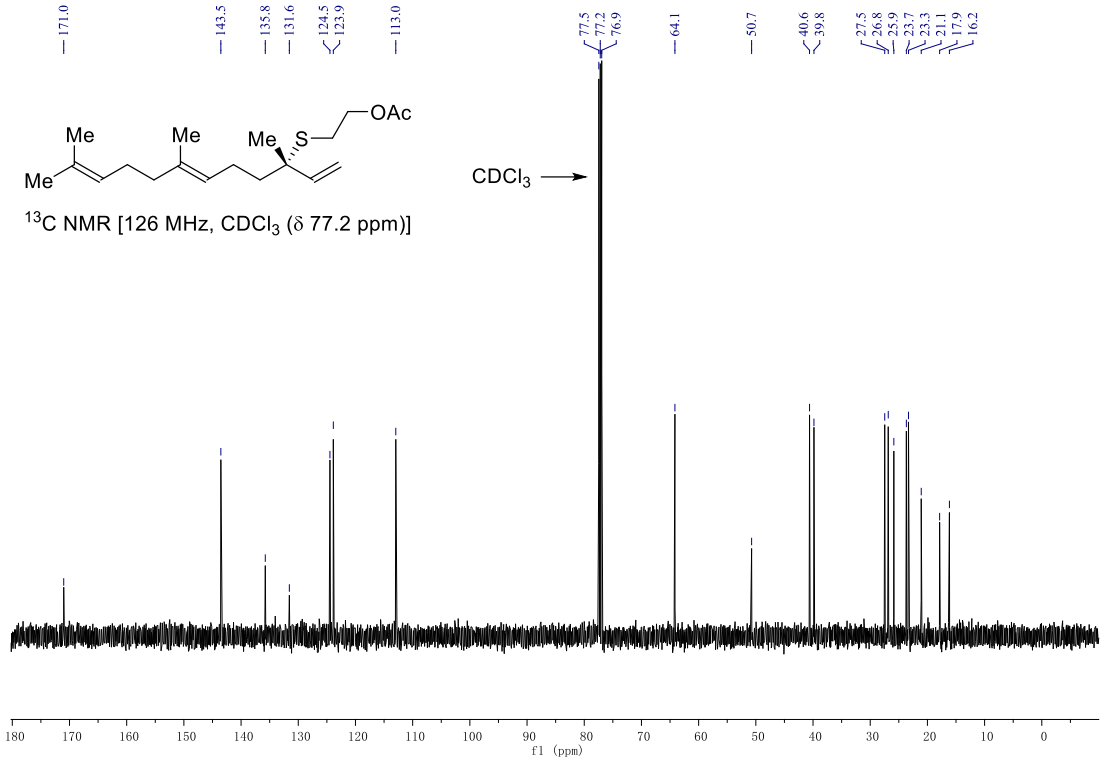
^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)]



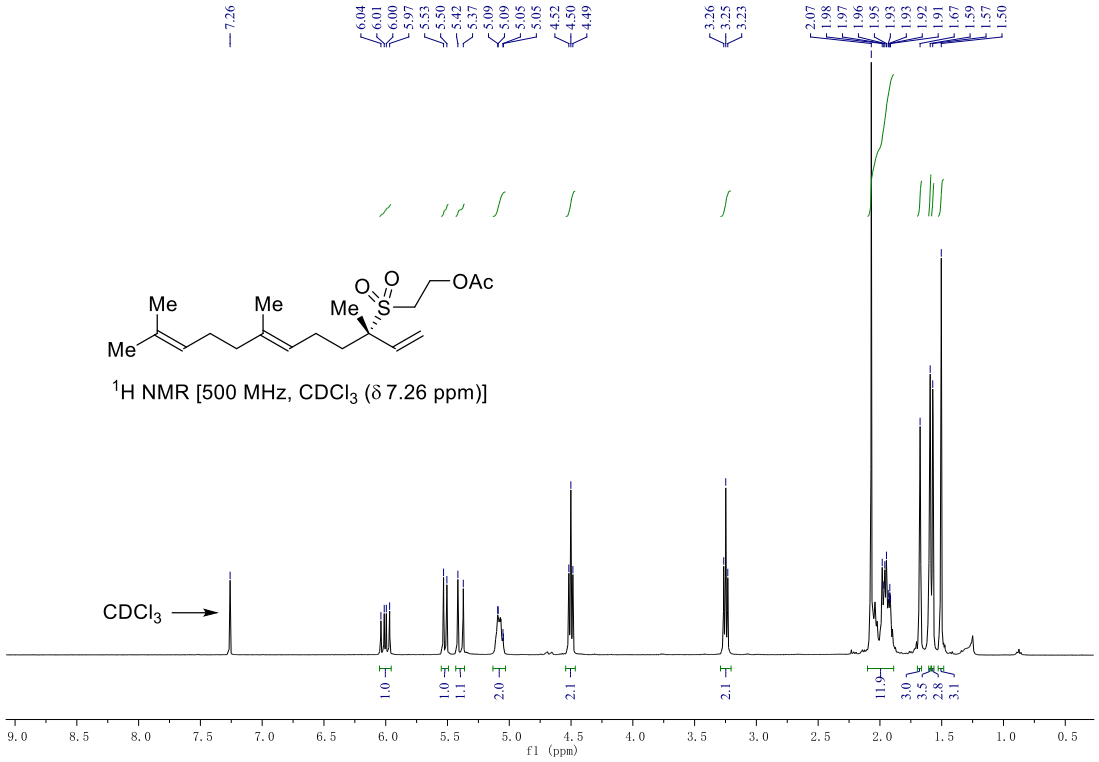
^{13}C NMR [101 MHz, $CDCl_3$ (δ 77.2 ppm)]

Compound 3ec

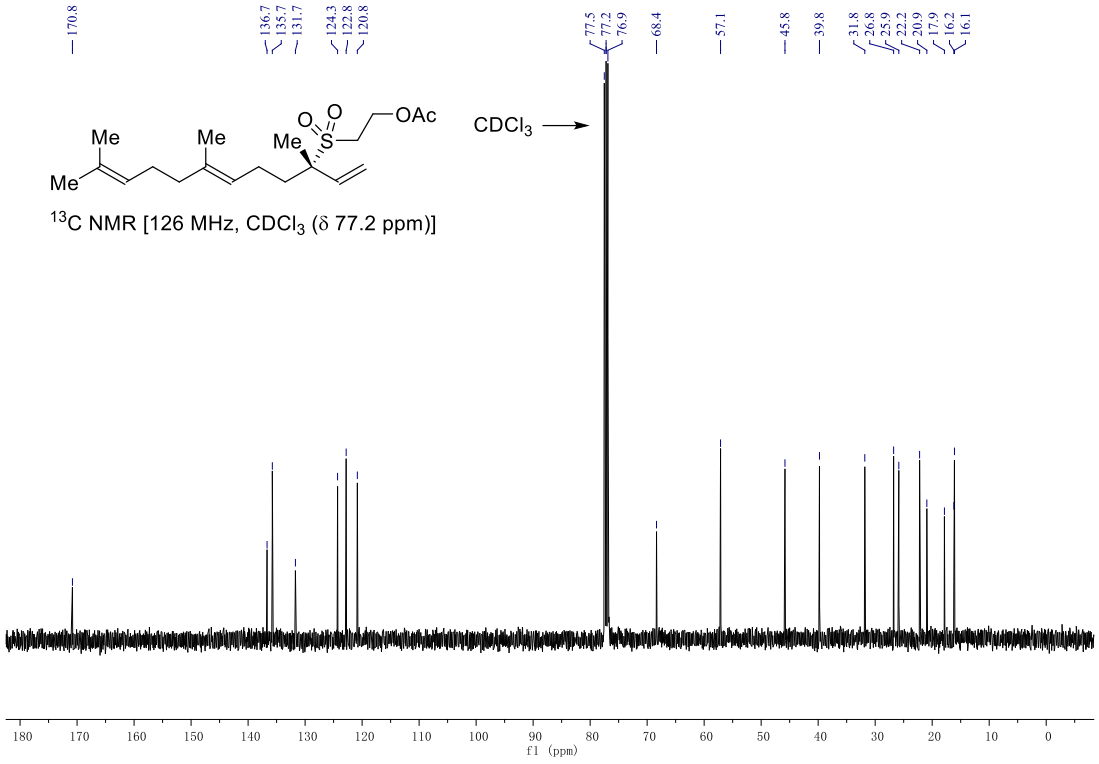




Compound 5

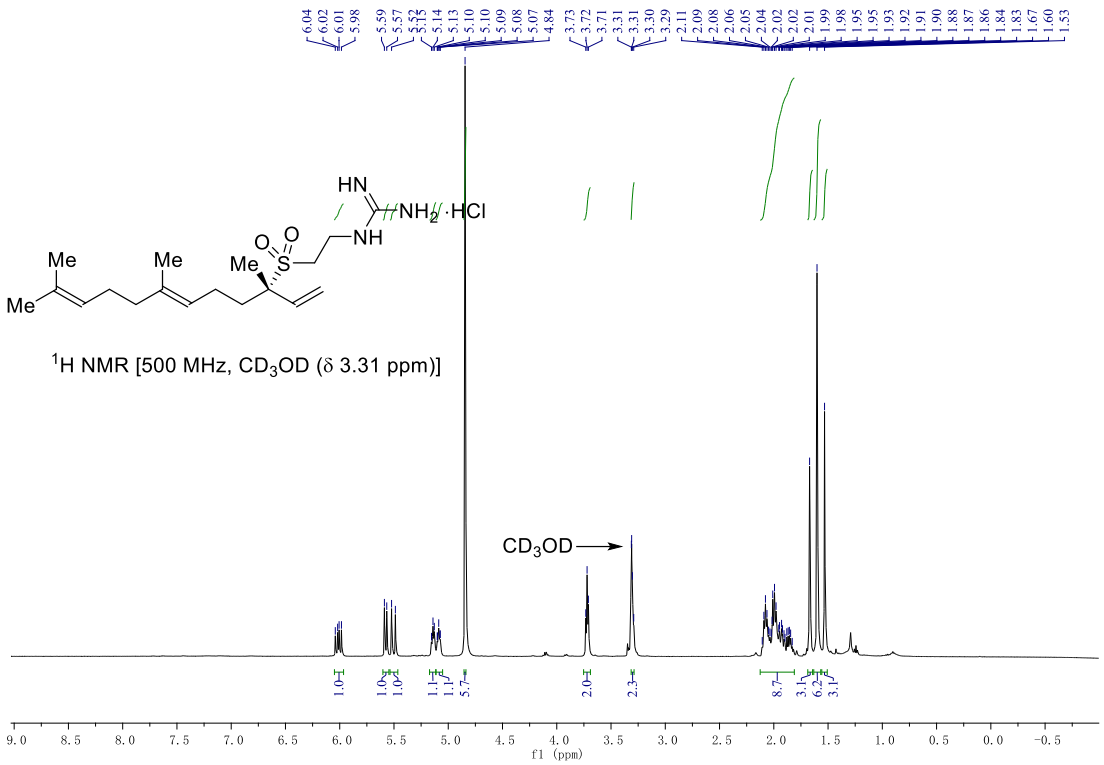


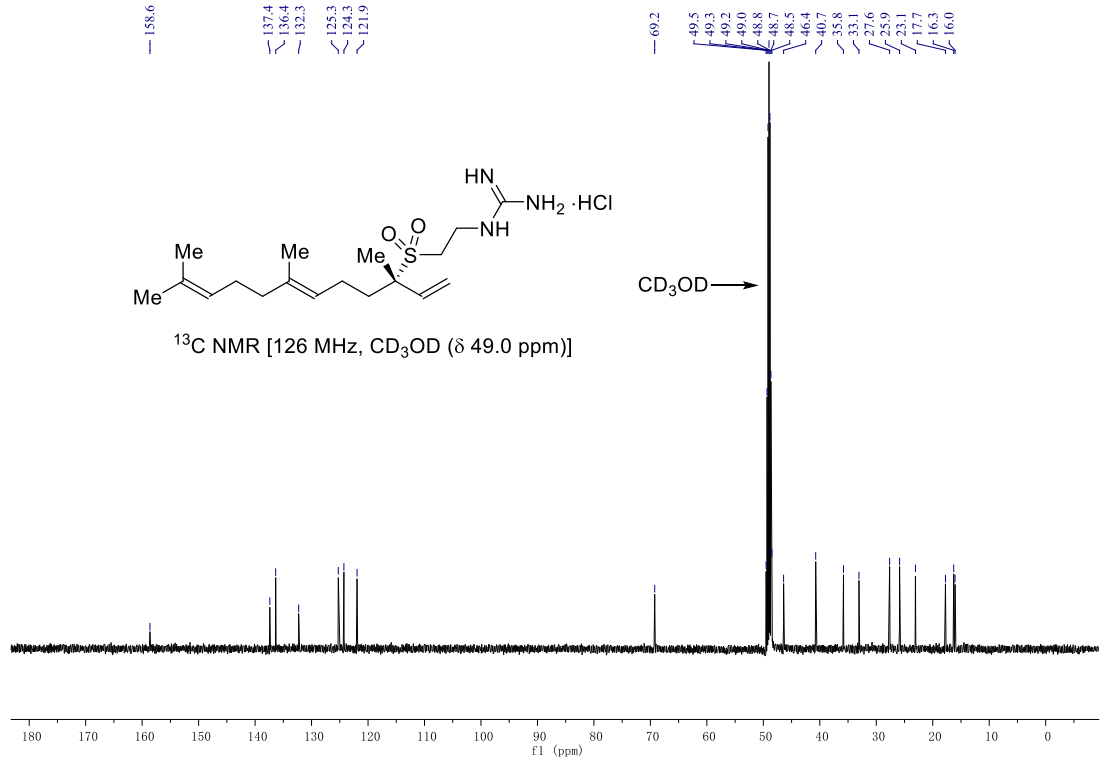
^{1}H NMR [500 MHz, $CDCl_3$ (δ 7.26 ppm)]



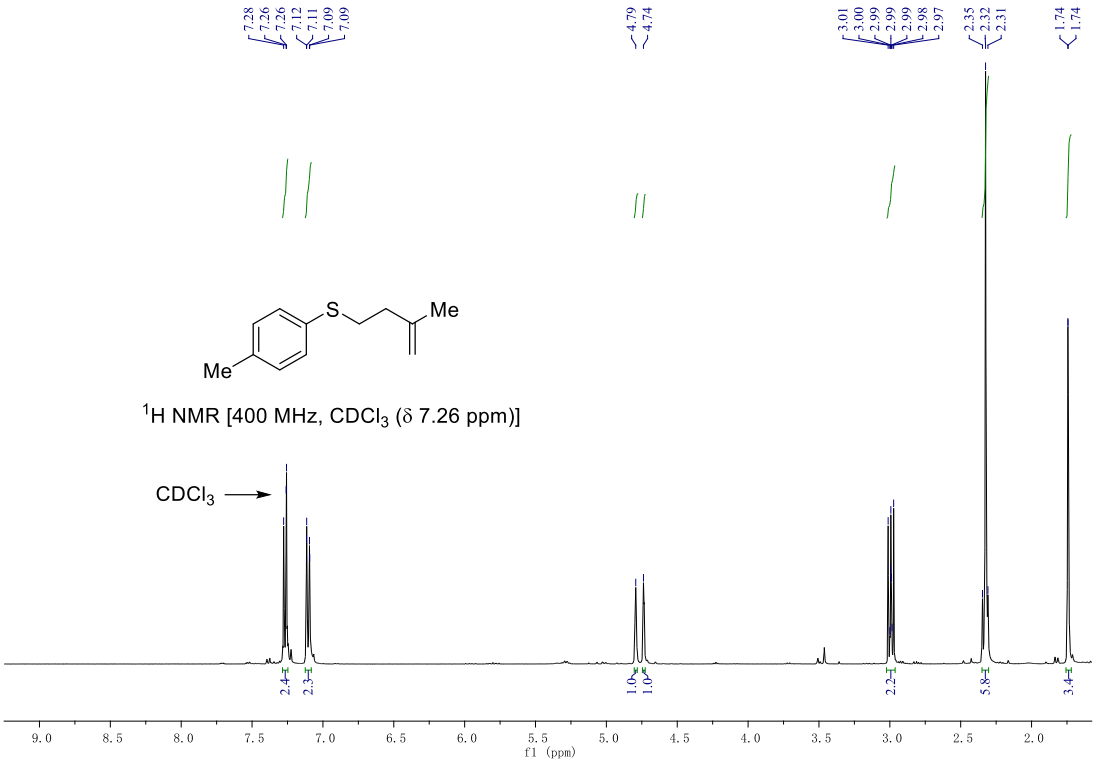
^{13}C NMR [126 MHz, $CDCl_3$ (δ 77.2 ppm)]

(–)-agelasidine A hydrogen chloride 4

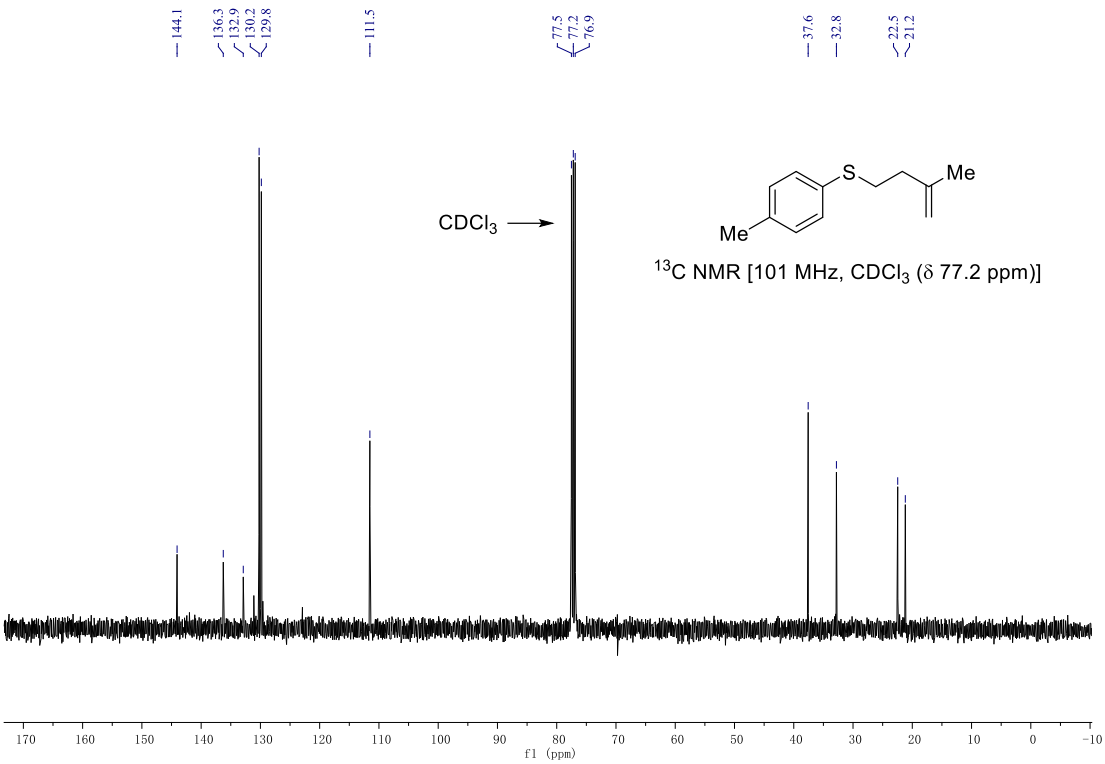




(3-methylbut-3-en-1-yl)(*p*-tolyl)sulfane (6fd)

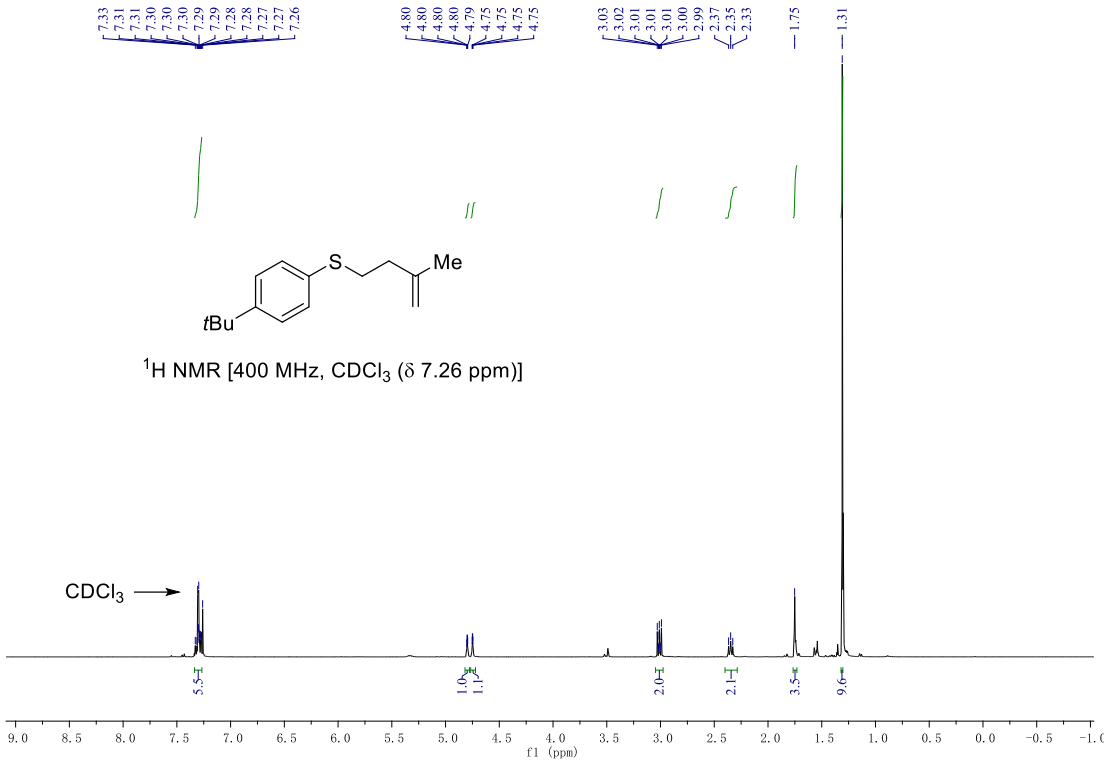


^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)]

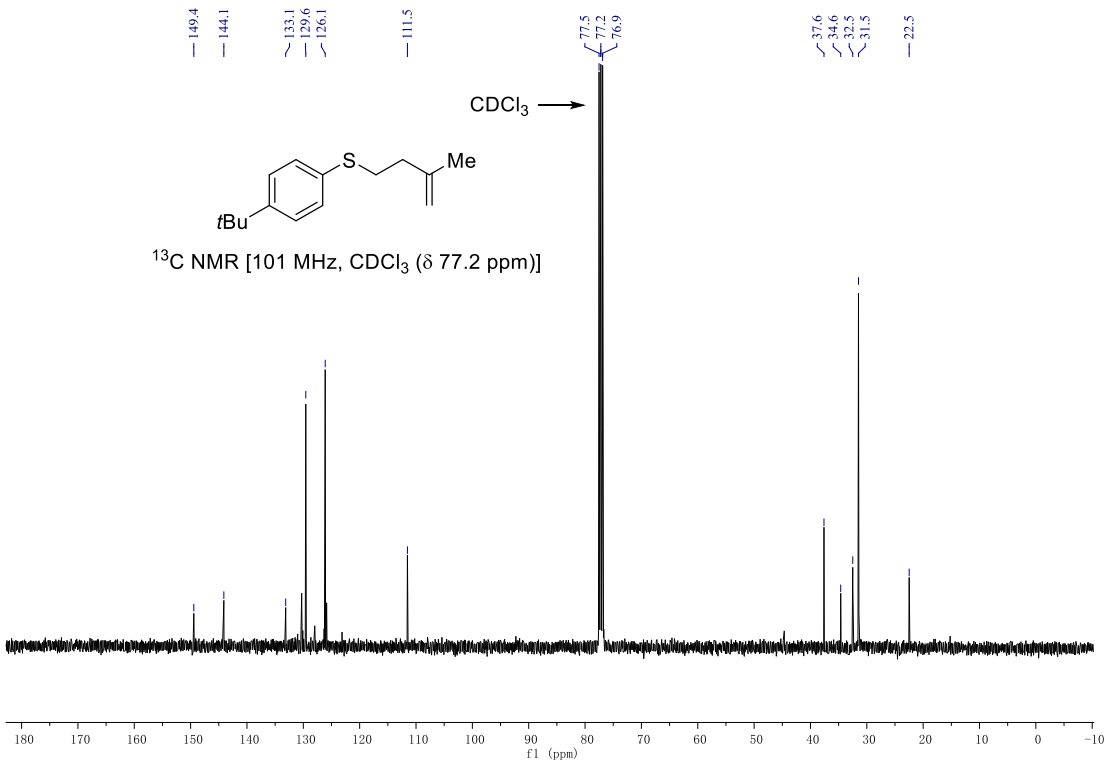


^{13}C NMR [101 MHz, $CDCl_3$ (δ 77.2 ppm)]

(4-(*tert*-butyl)phenyl)(3-methylbut-3-en-1-yl)sulfane (6gd)

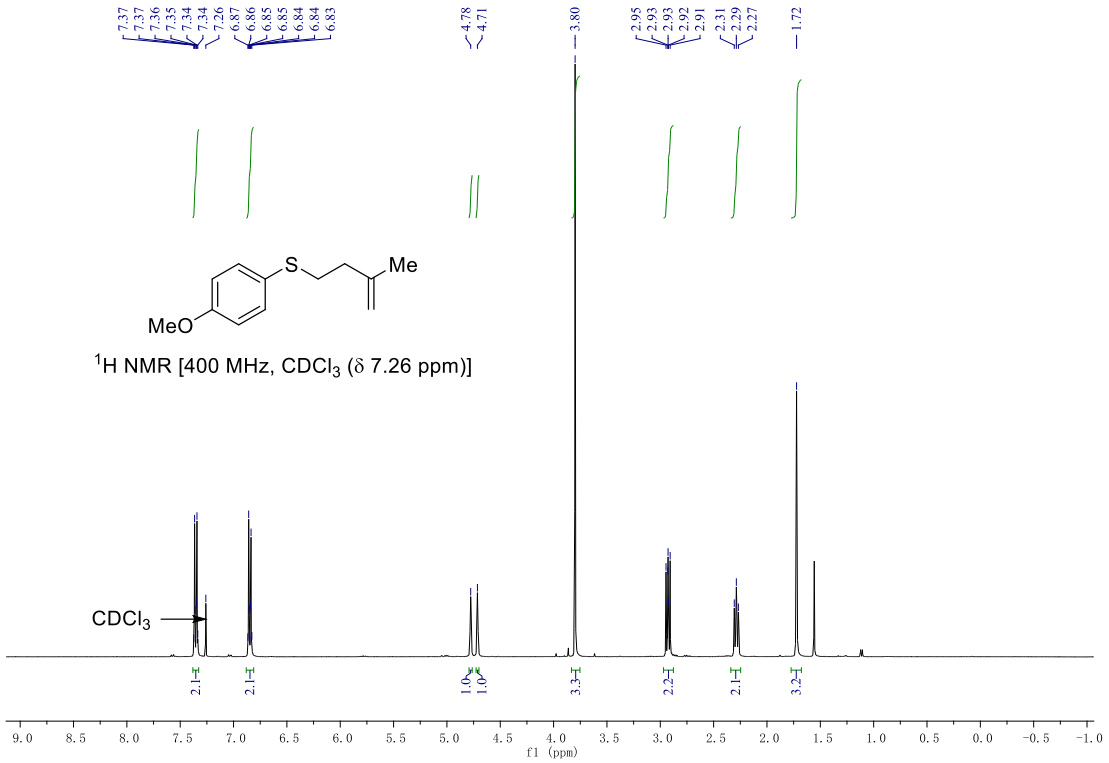


^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)]

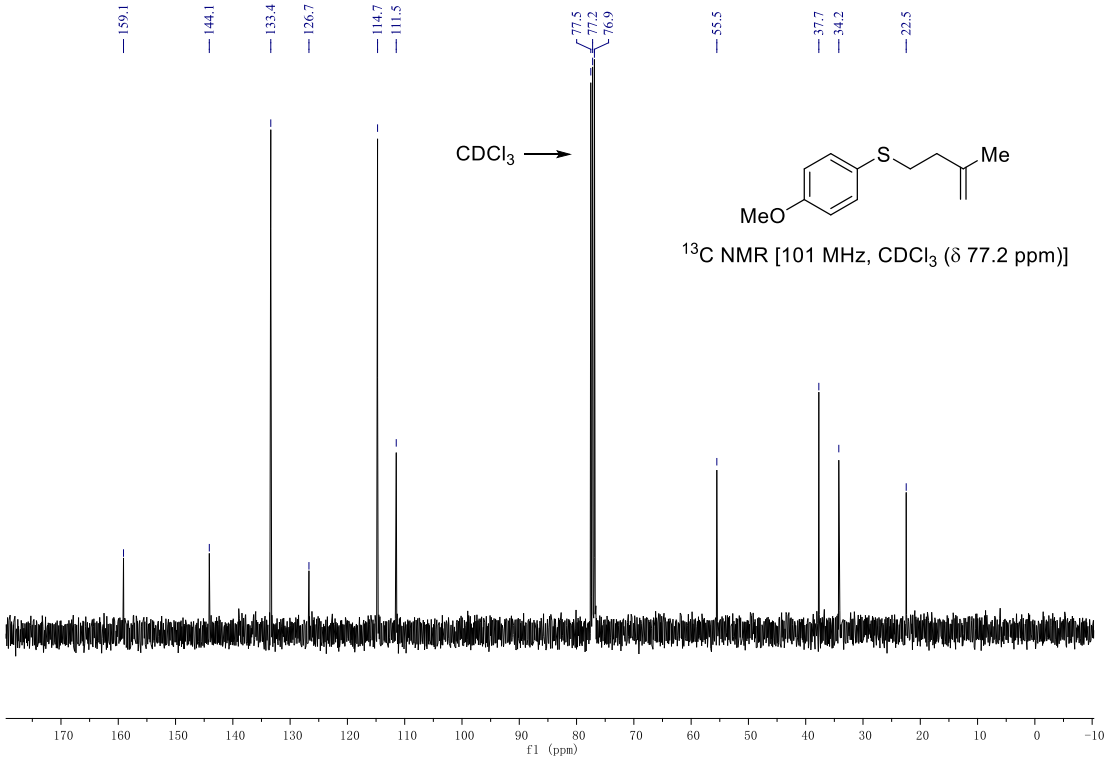


^{13}C NMR [101 MHz, $CDCl_3$ (δ 77.2 ppm)]

(4-methoxyphenyl)(3-methylbut-3-en-1-yl)sulfane (6hd)

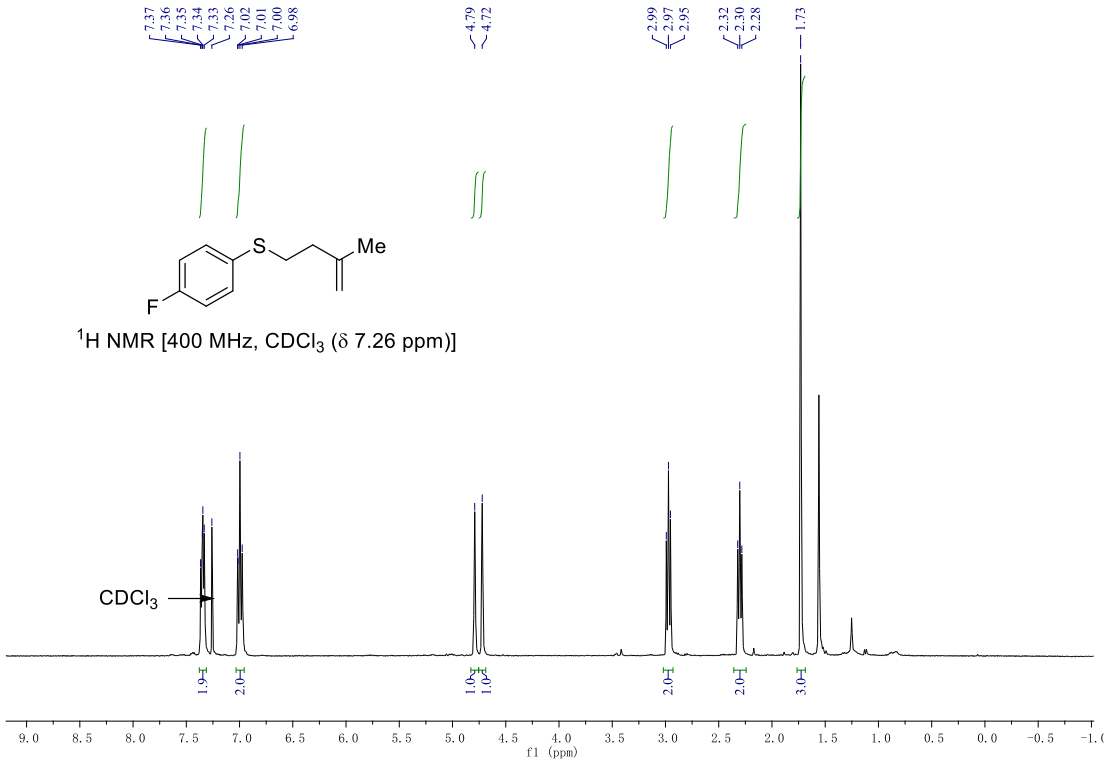


^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)]

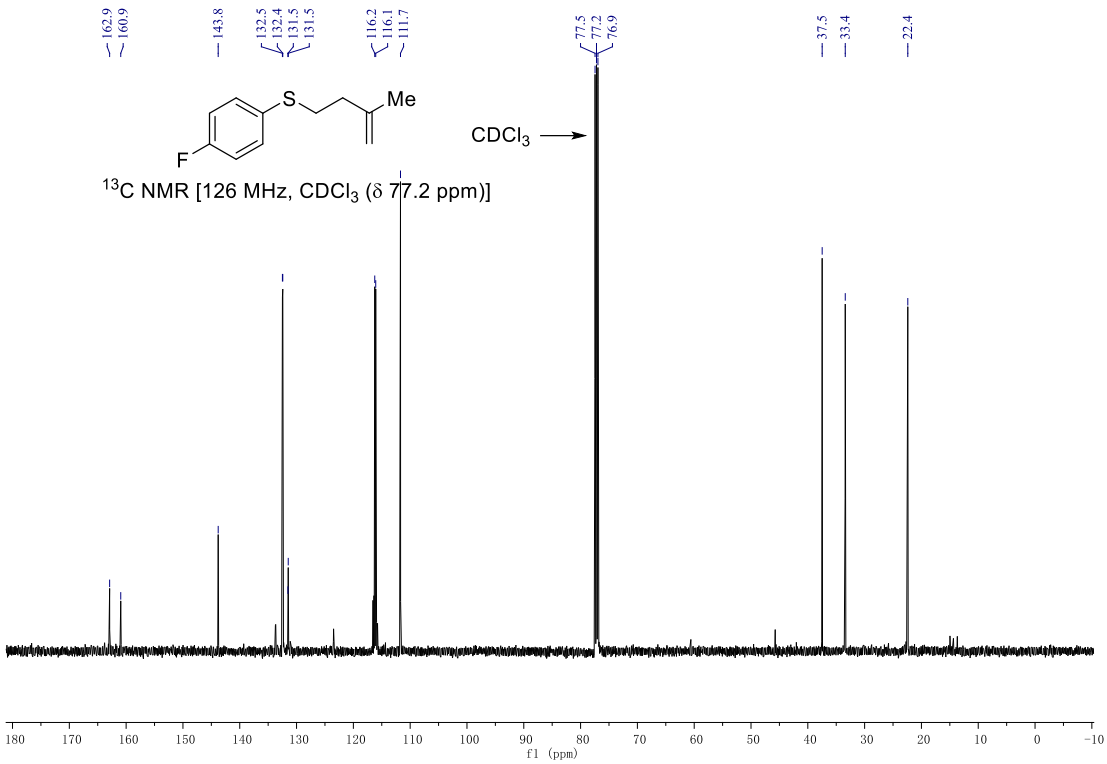


^{13}C NMR [101 MHz, $CDCl_3$ (δ 77.2 ppm)]

(4-fluorophenyl)(3-methylbut-3-en-1-yl)sulfane (6id)

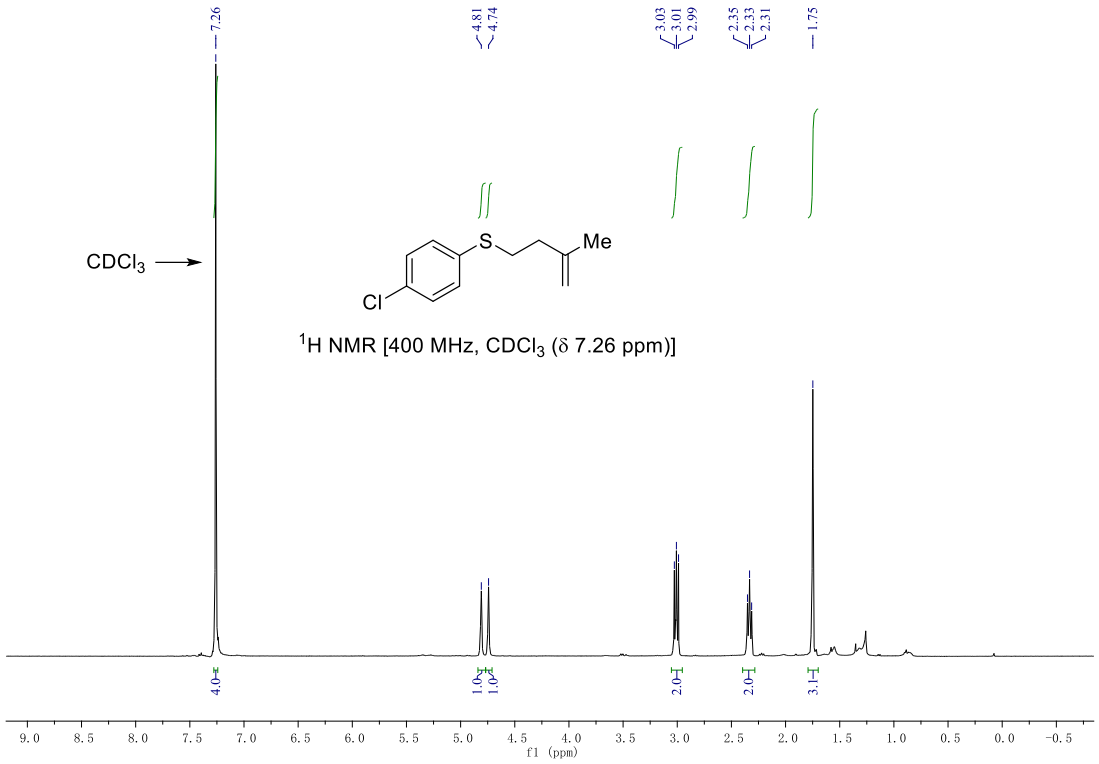


^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)]

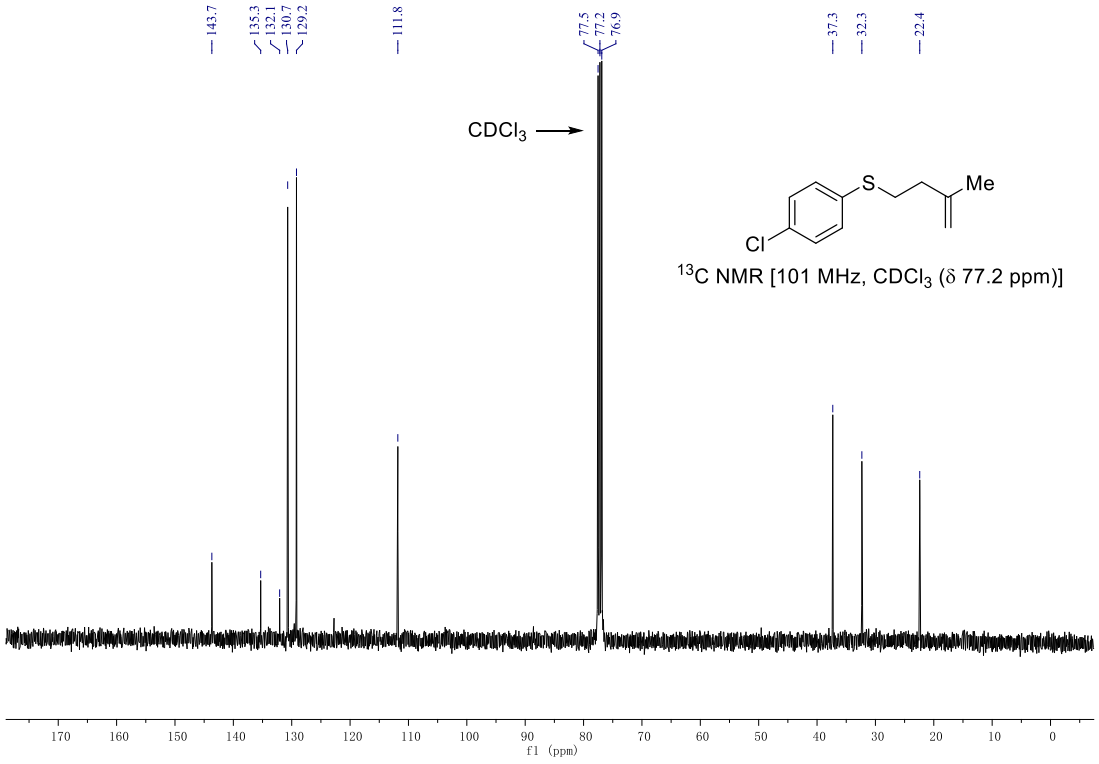


^{13}C NMR [126 MHz, $CDCl_3$ (δ 77.2 ppm)]

(4-chlorophenyl)(3-methylbut-3-en-1-yl)sulfane (6jd)

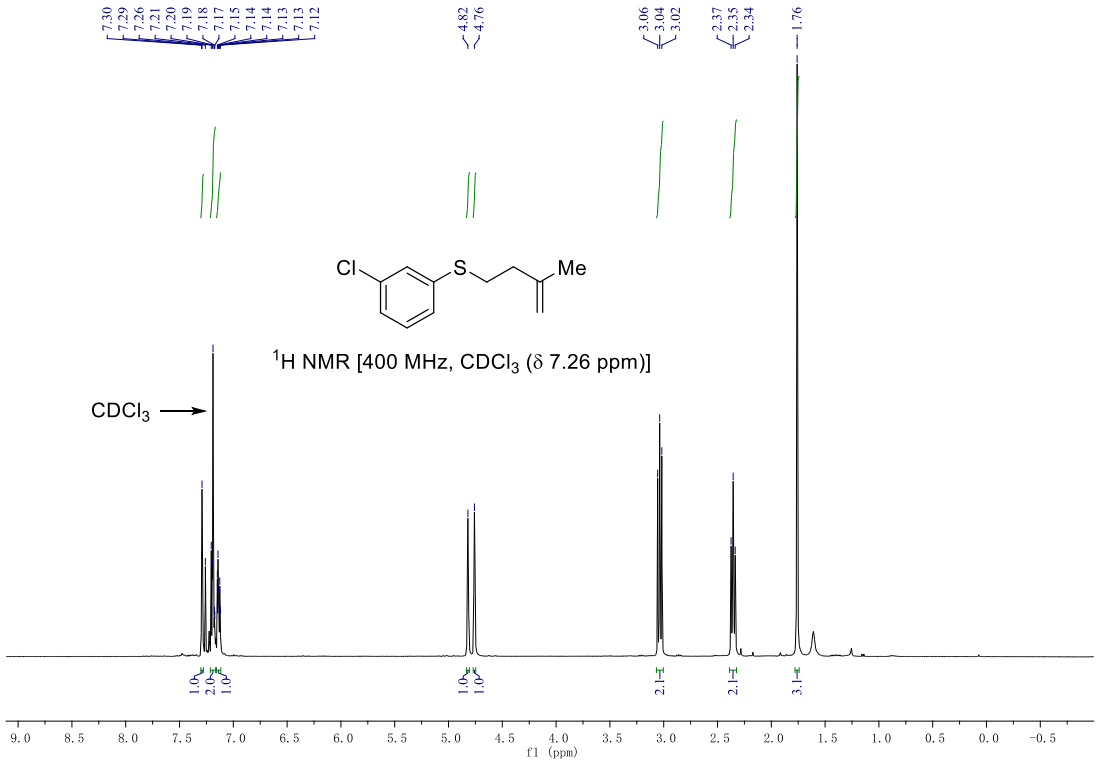


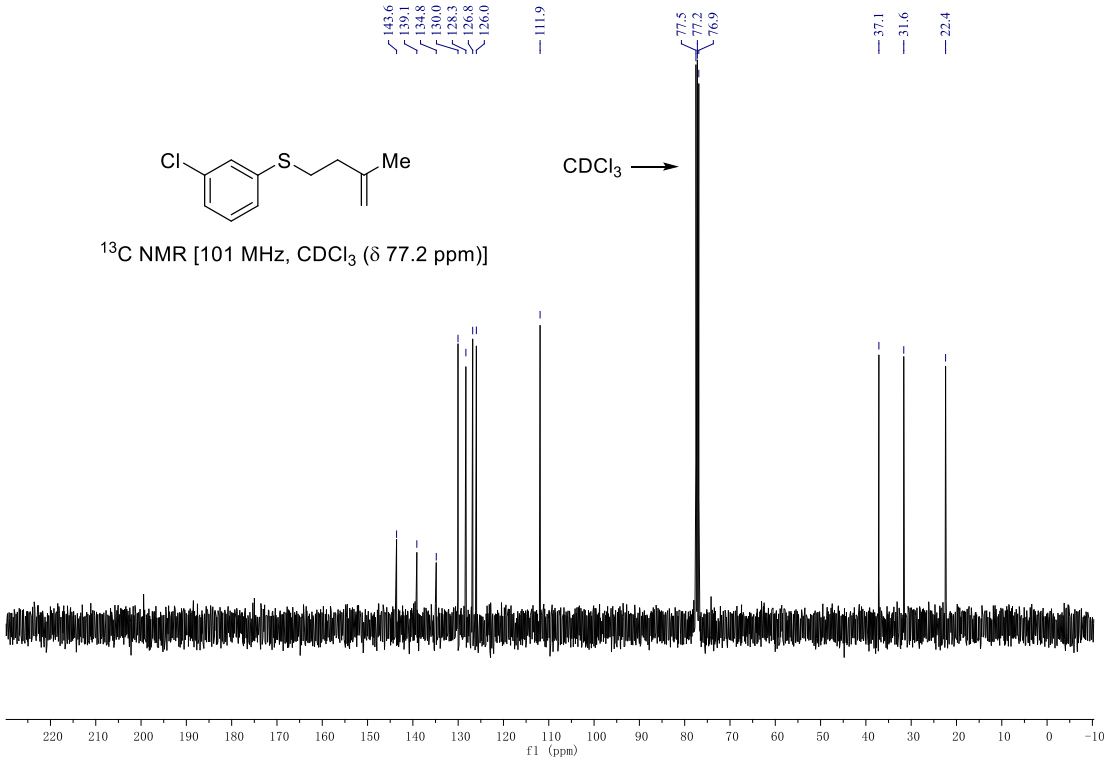
^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)]



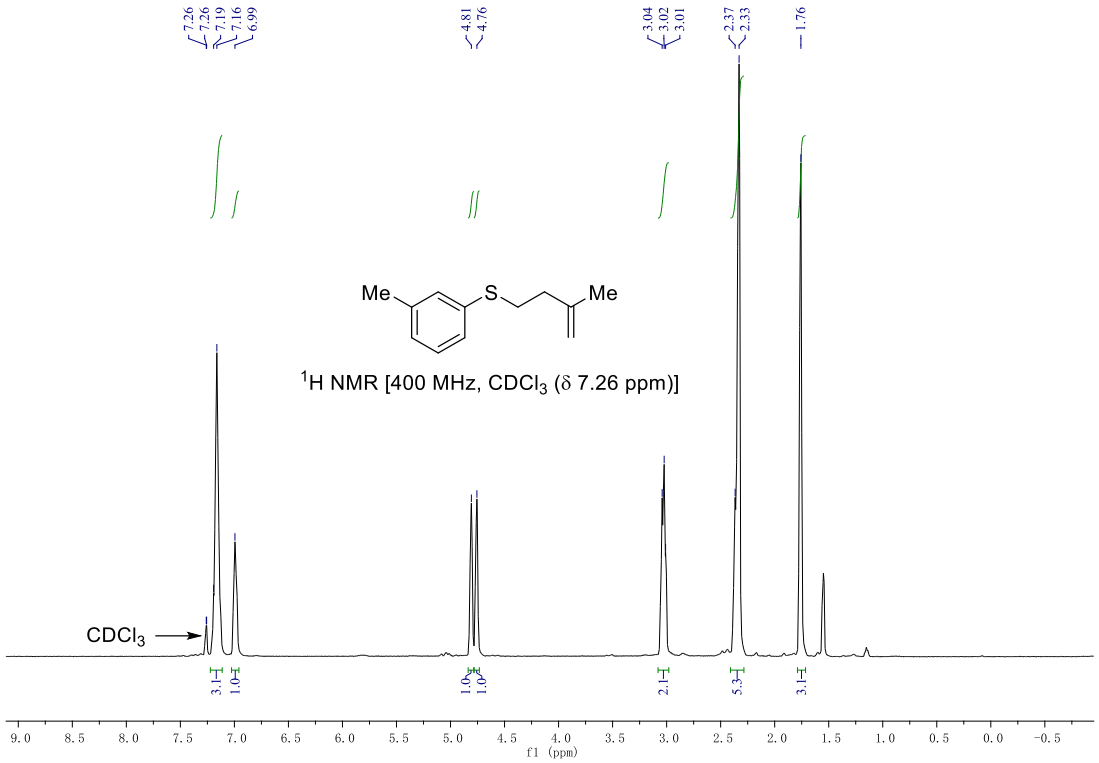
^{13}C NMR [101 MHz, $CDCl_3$ (δ 77.2 ppm)]

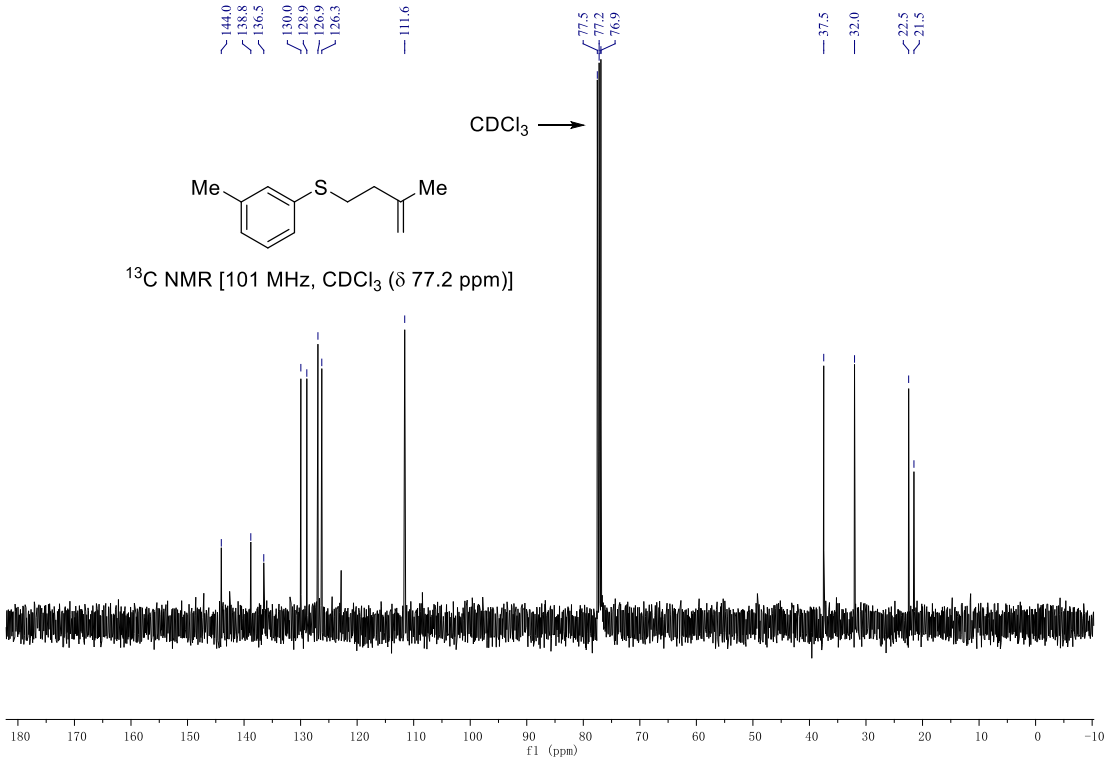
(3-chlorophenyl)(3-methylbut-3-en-1-yl)sulfane (6kd)



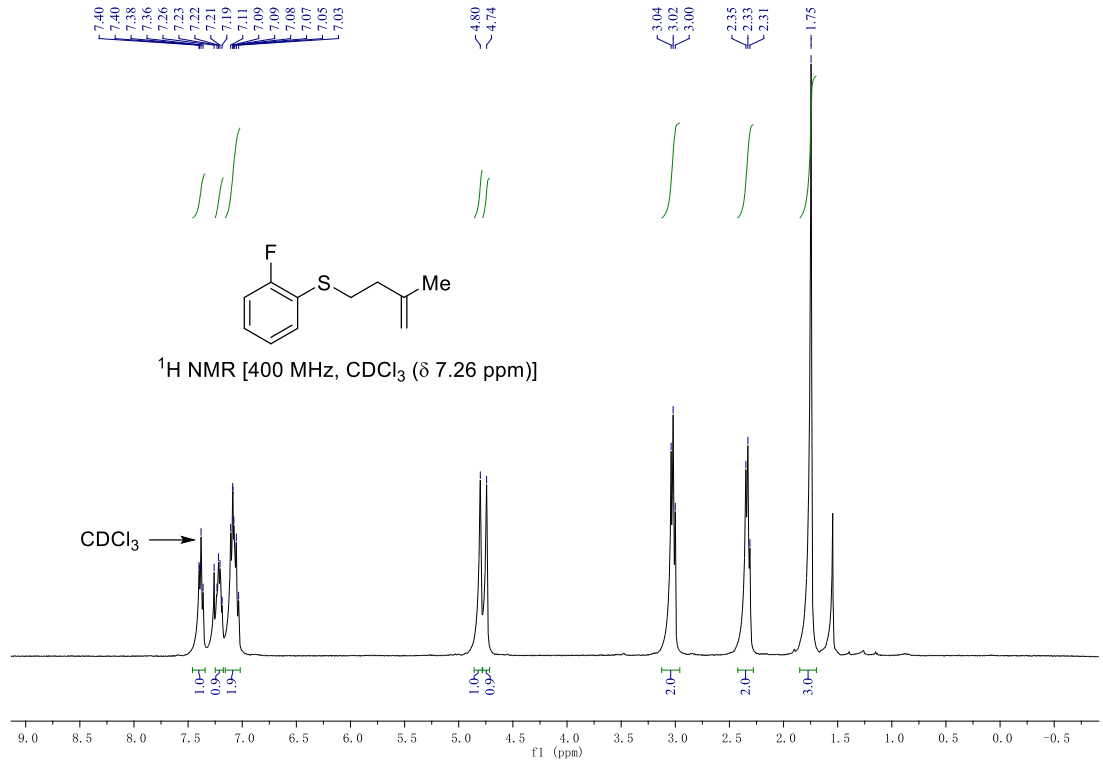


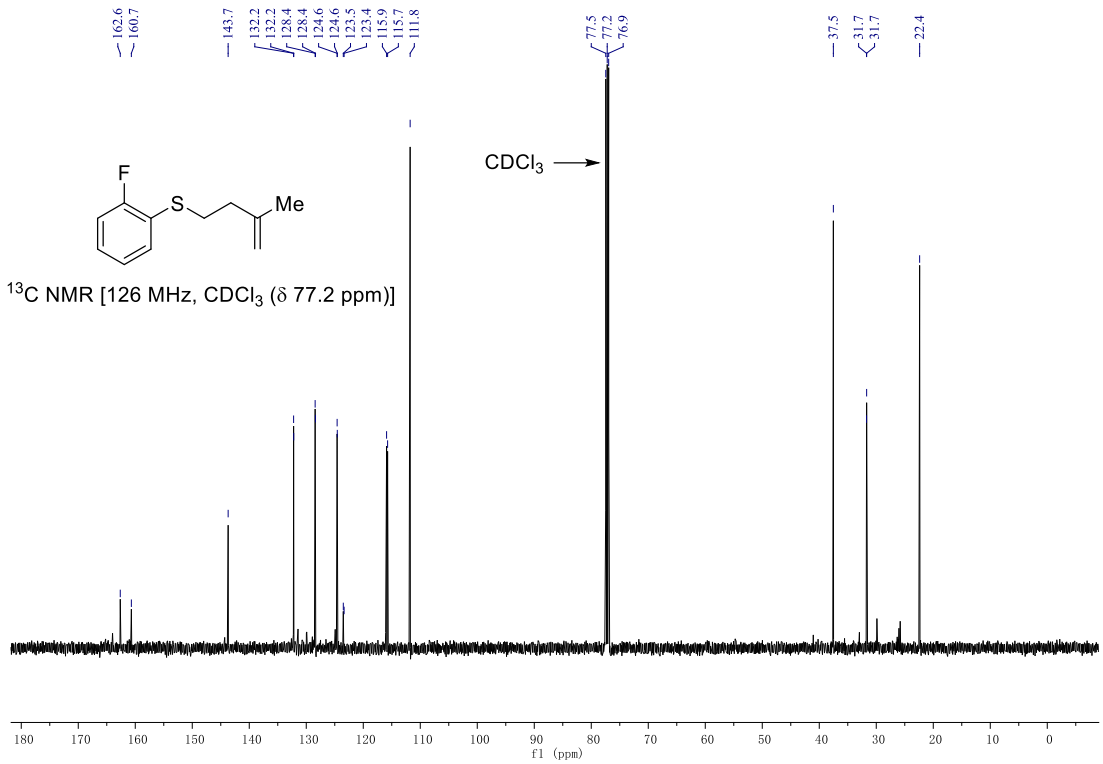
(3-methylbut-3-en-1-yl)(*m*-tolyl)sulfane (6ld)





(2-fluorophenyl)(3-methylbut-3-en-1-yl)sulfane (6md)





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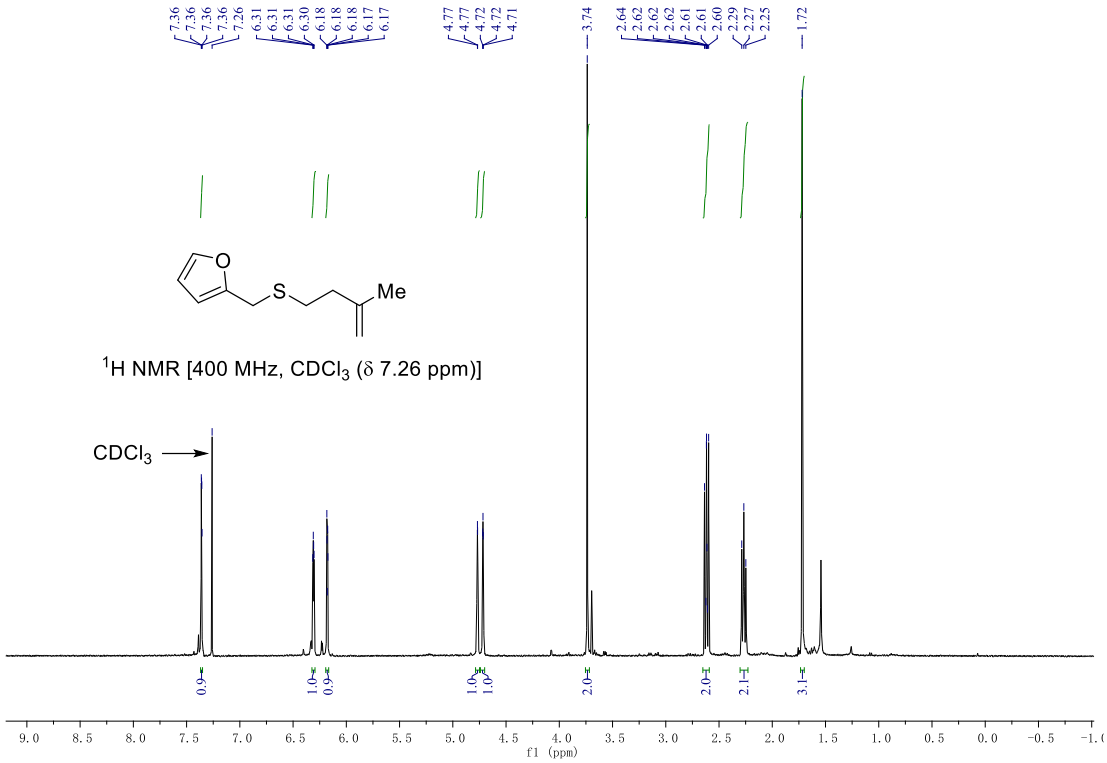
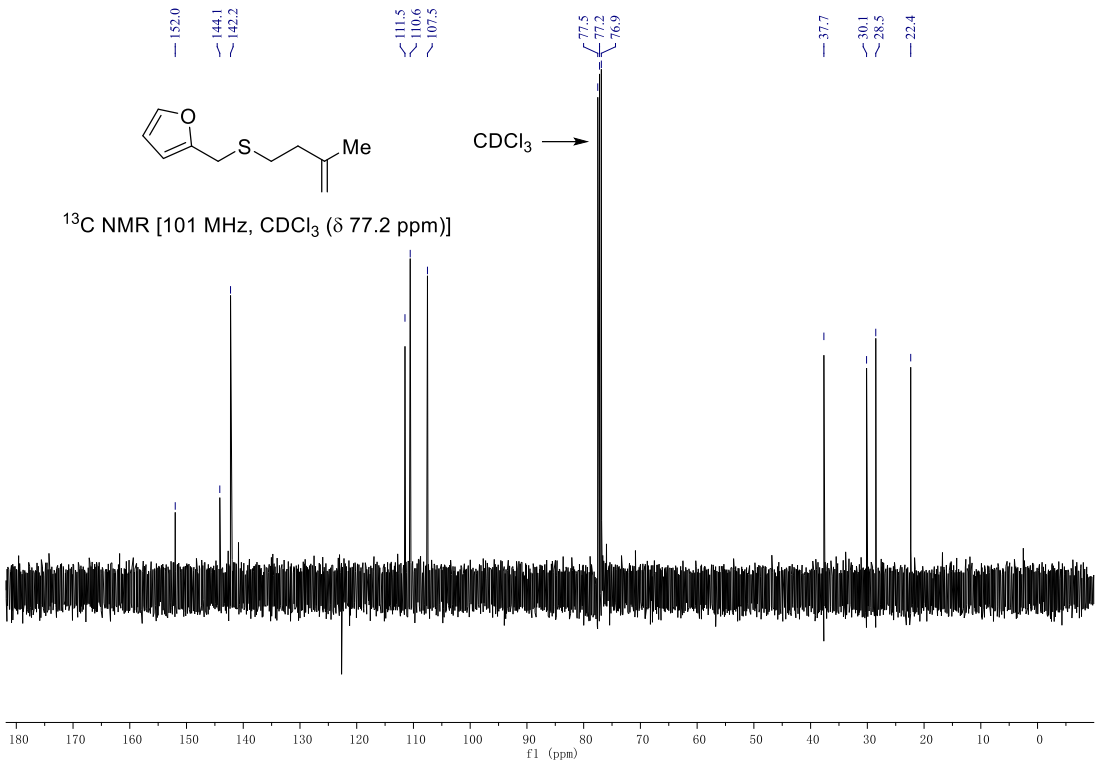
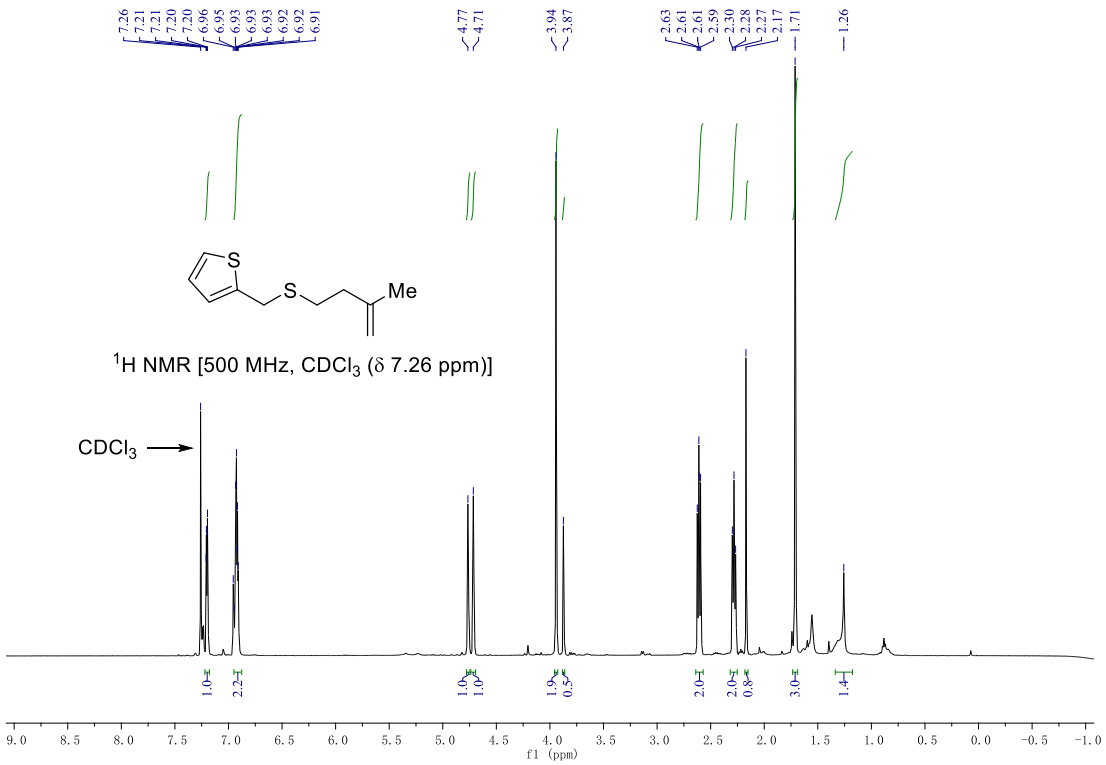
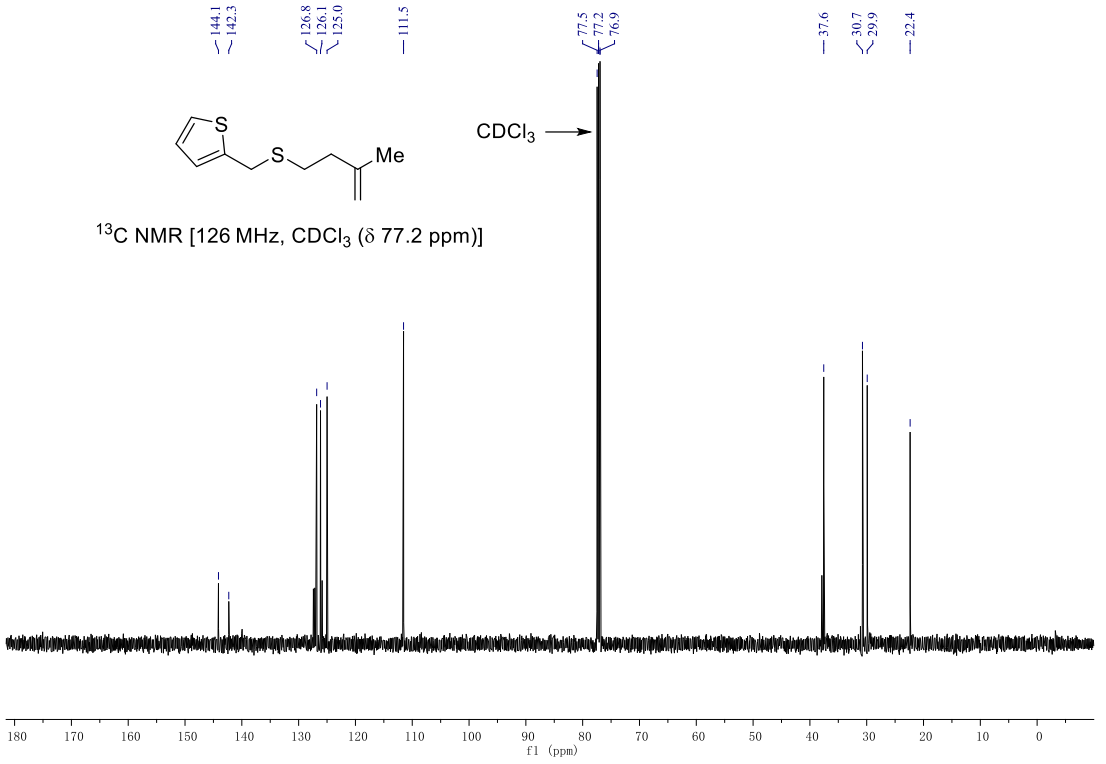


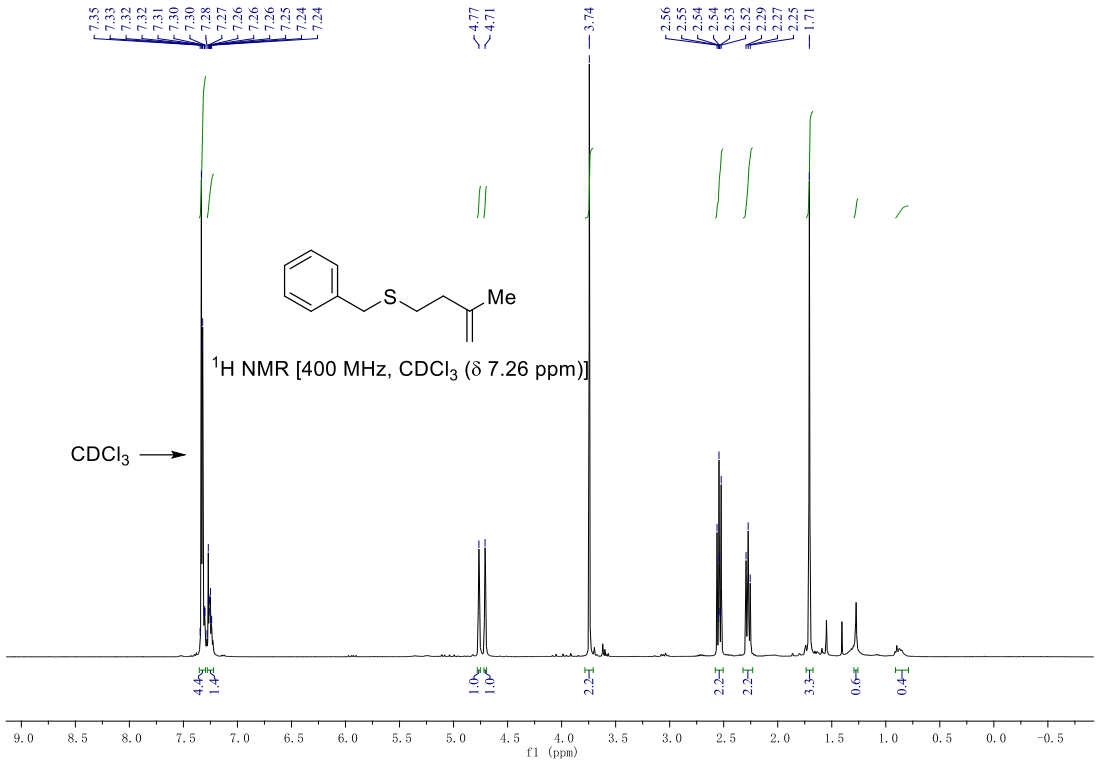


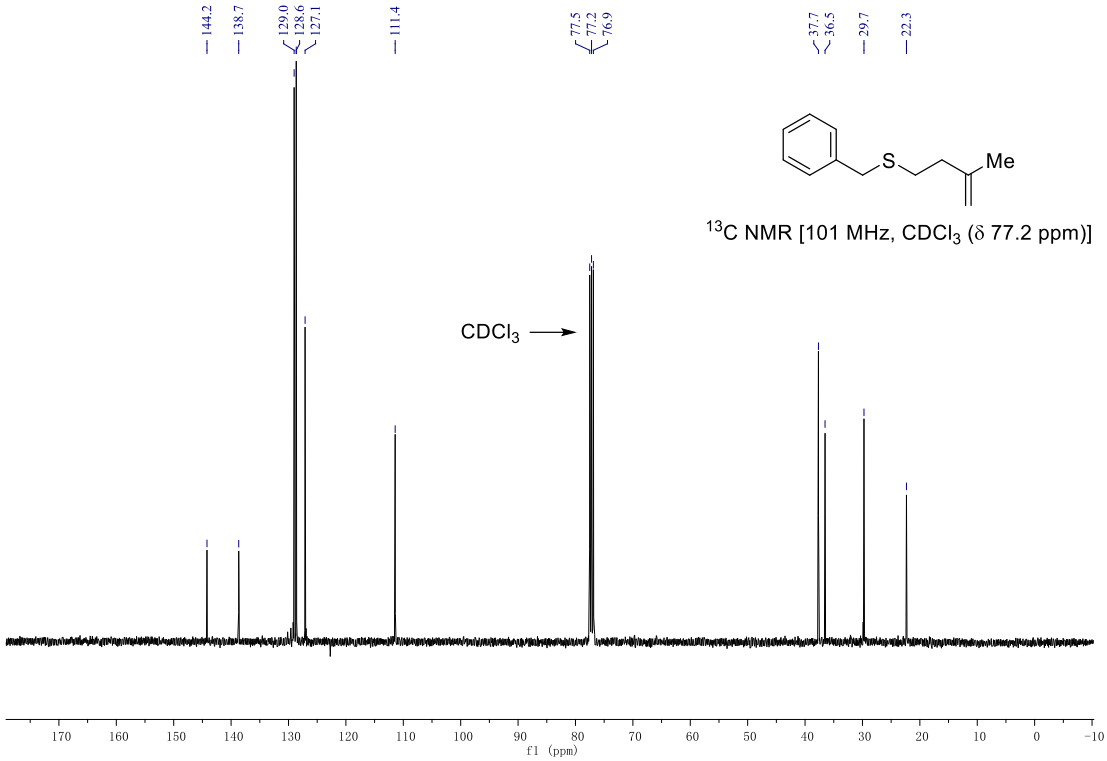
2-(((3-methylbut-3-en-1-yl)thio)methyl)thiophene (6od)



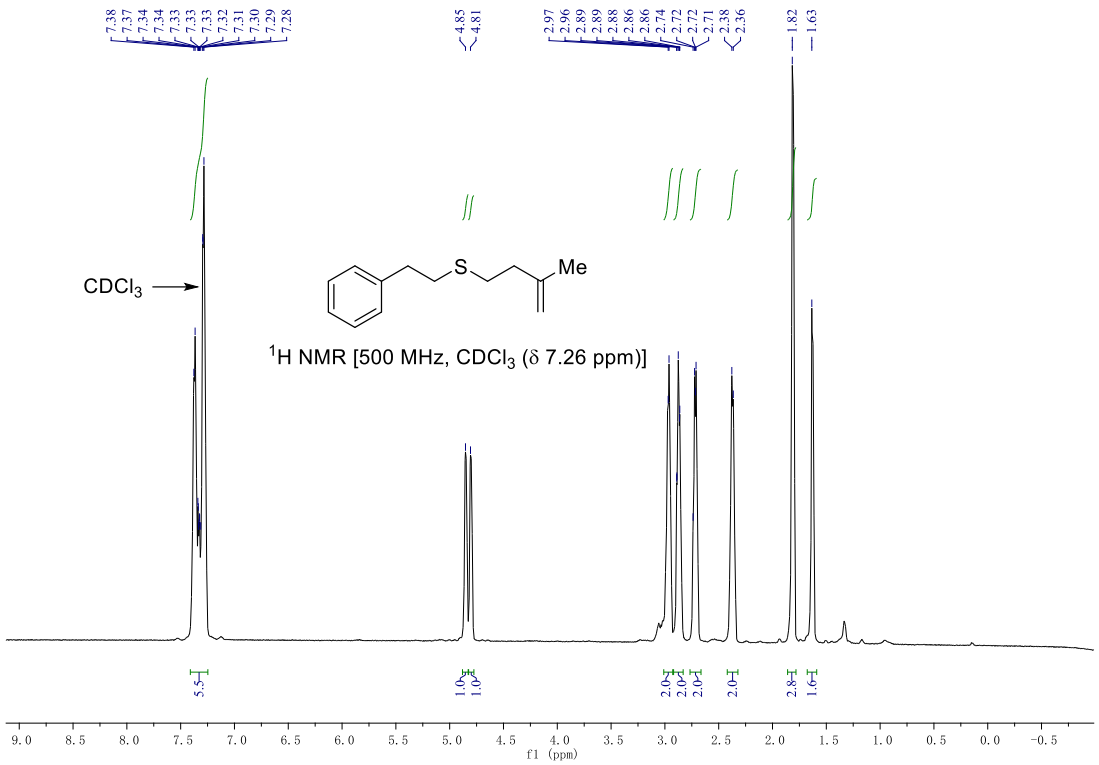


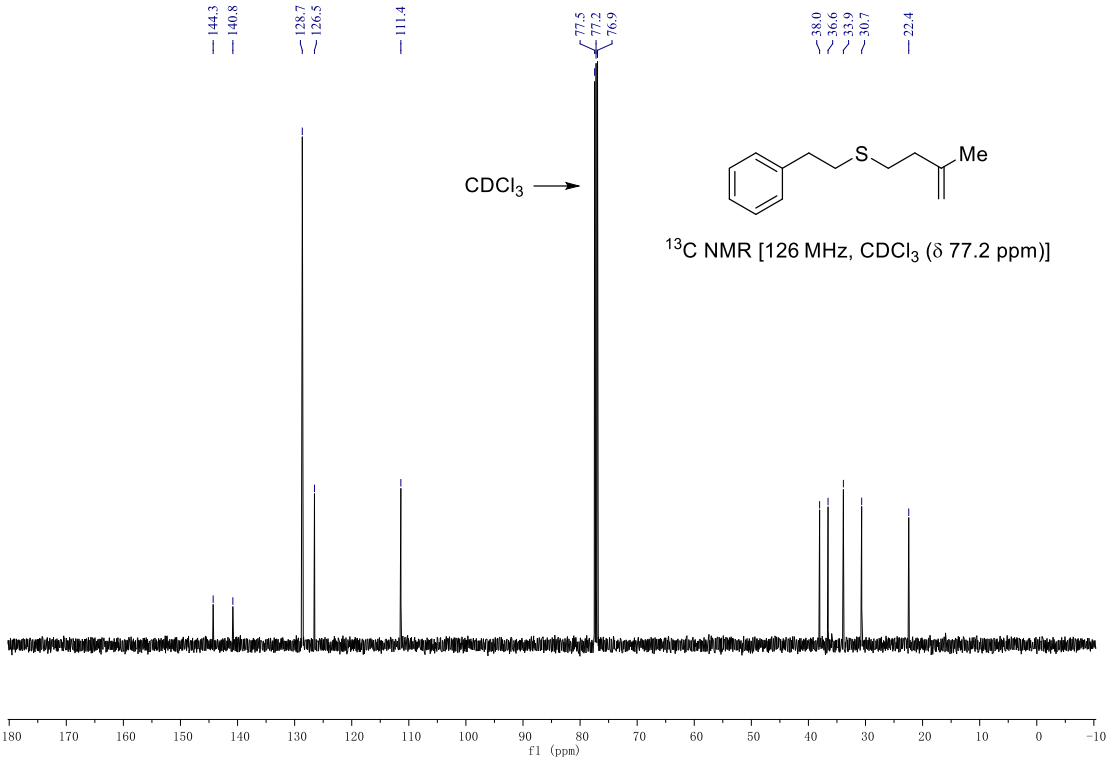
benzyl(3-methylbut-3-en-1-yl)sulfane (6pd)



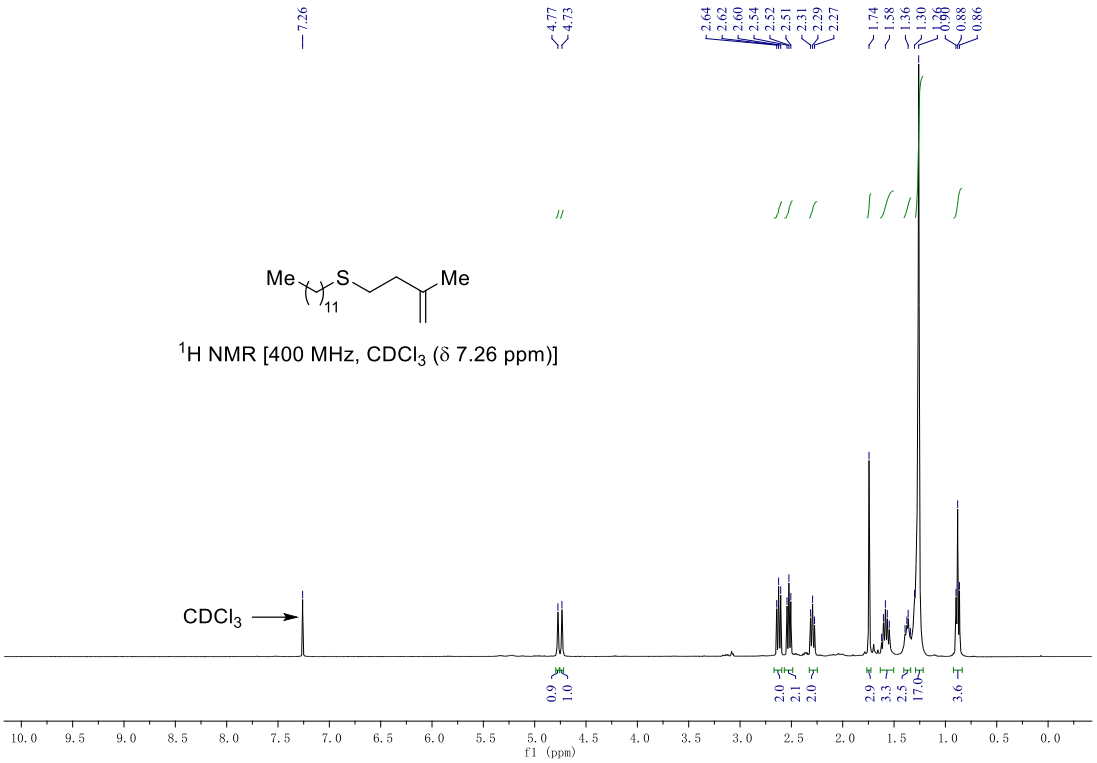


(3-methylbut-3-en-1-yl)(phenethyl)sulfane (6qd)

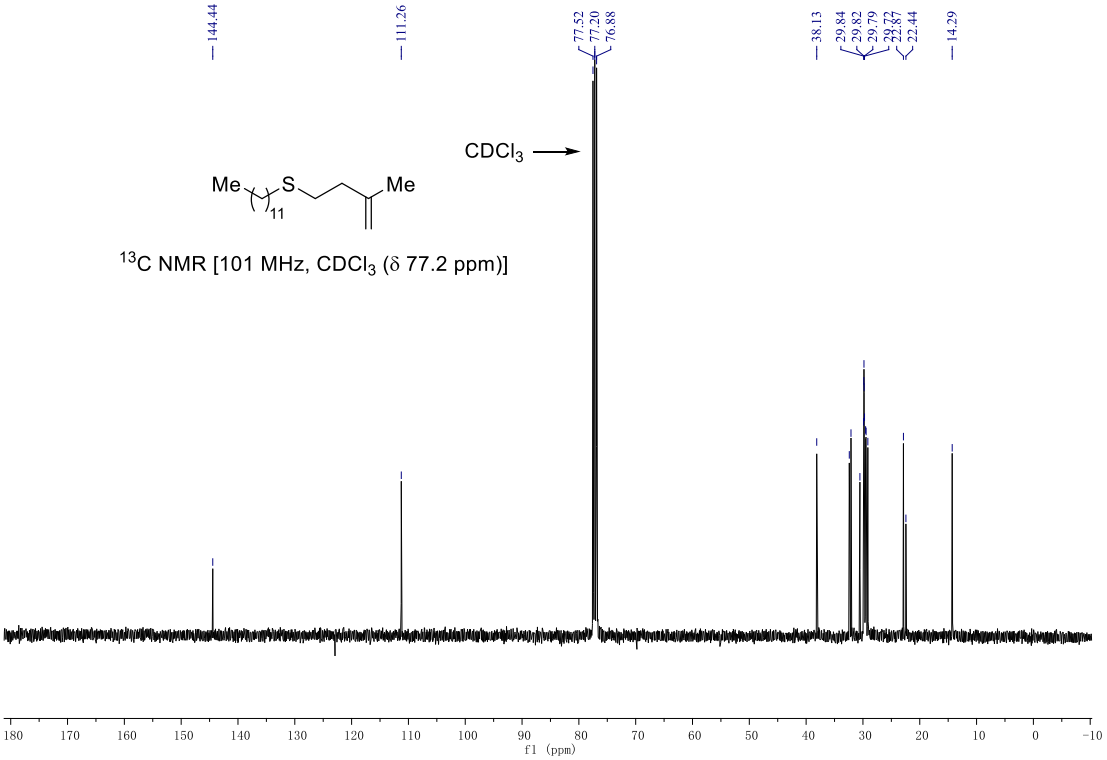




dodecyl(3-methylbut-3-en-1-yl)sulfane (6rd)

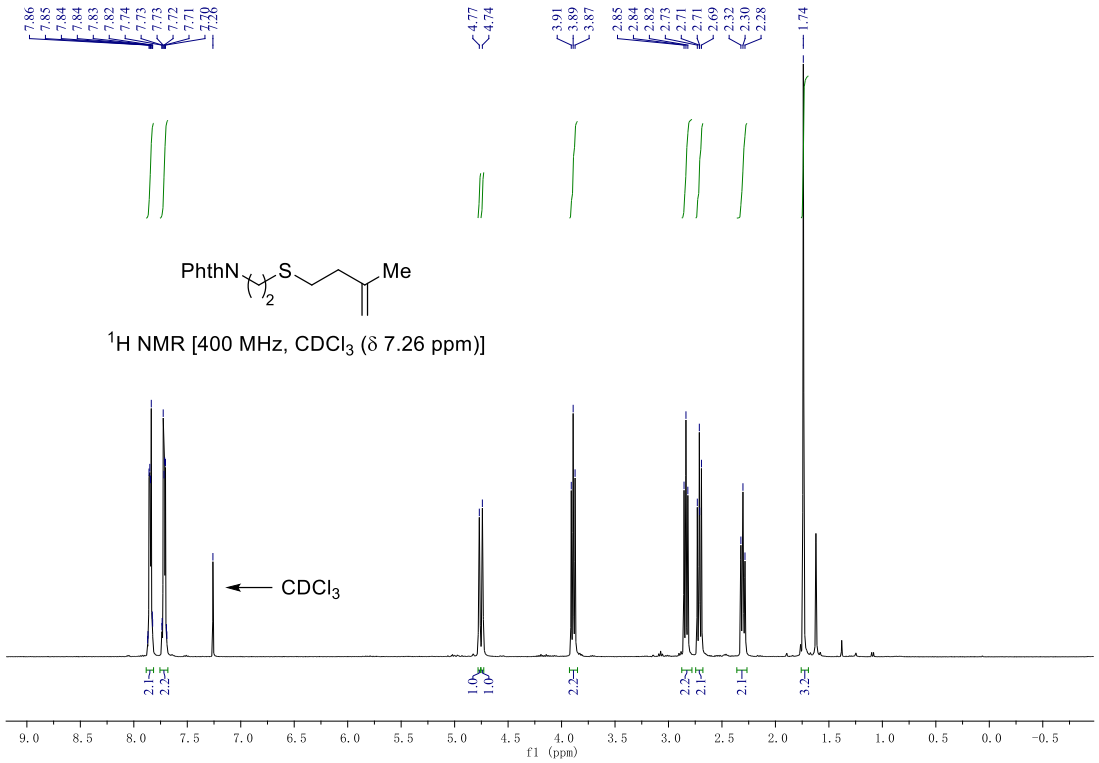


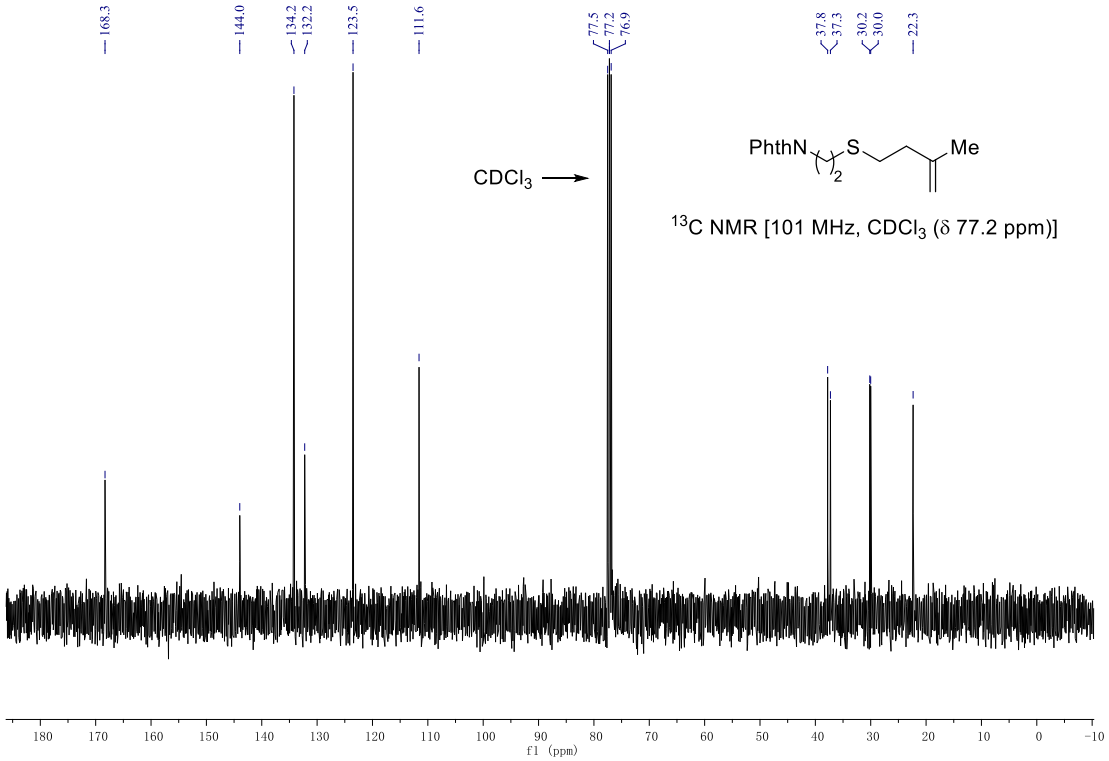
^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)]



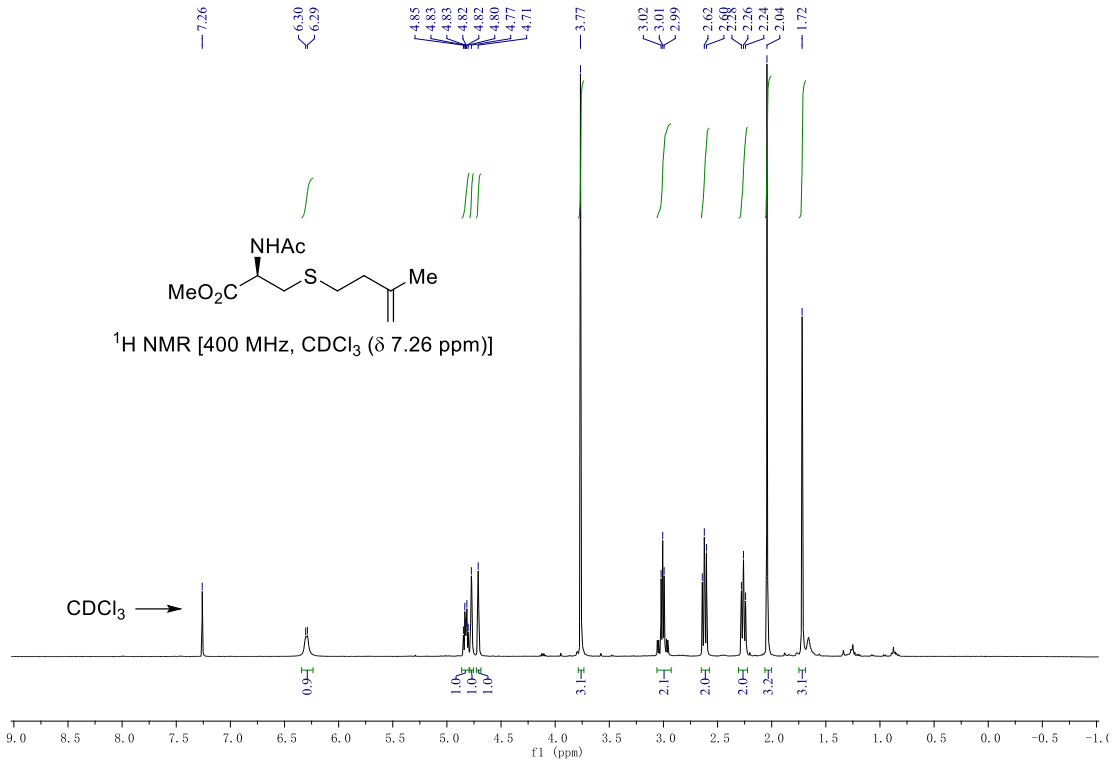
^{13}C NMR [101 MHz, $CDCl_3$ (δ 77.2 ppm)]

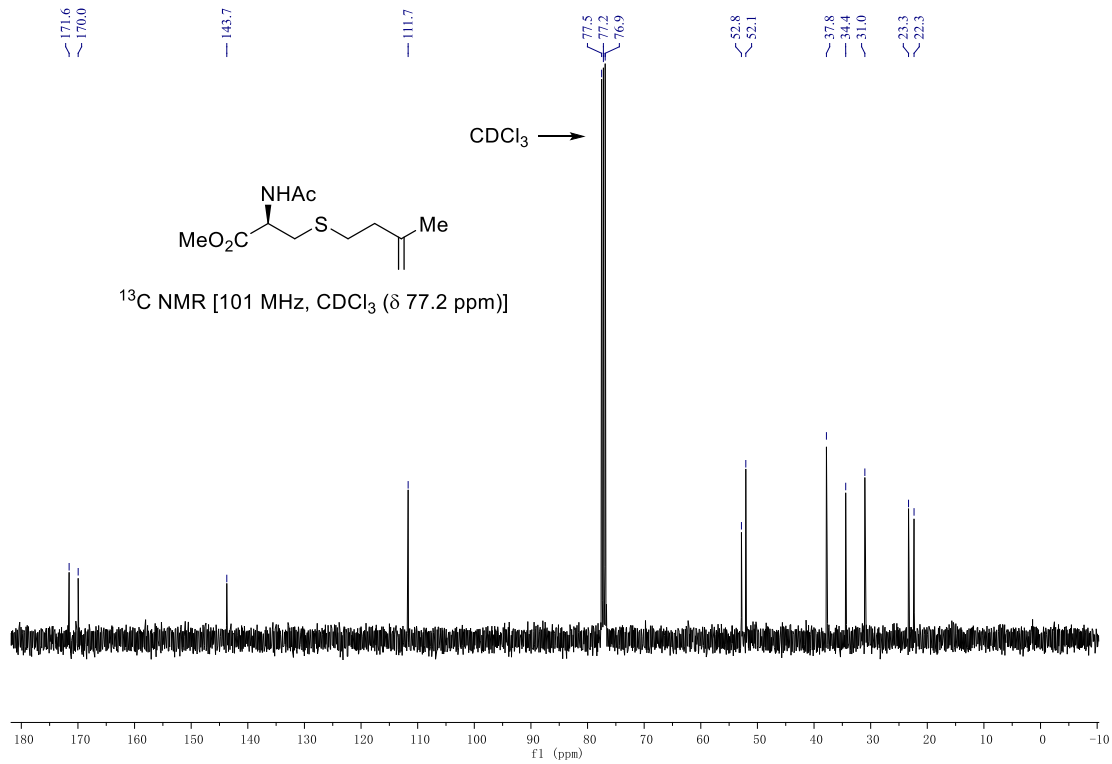
3-(2-((3-methylbut-3-en-1-yl)thio)ethyl)isoindoline (6sd)



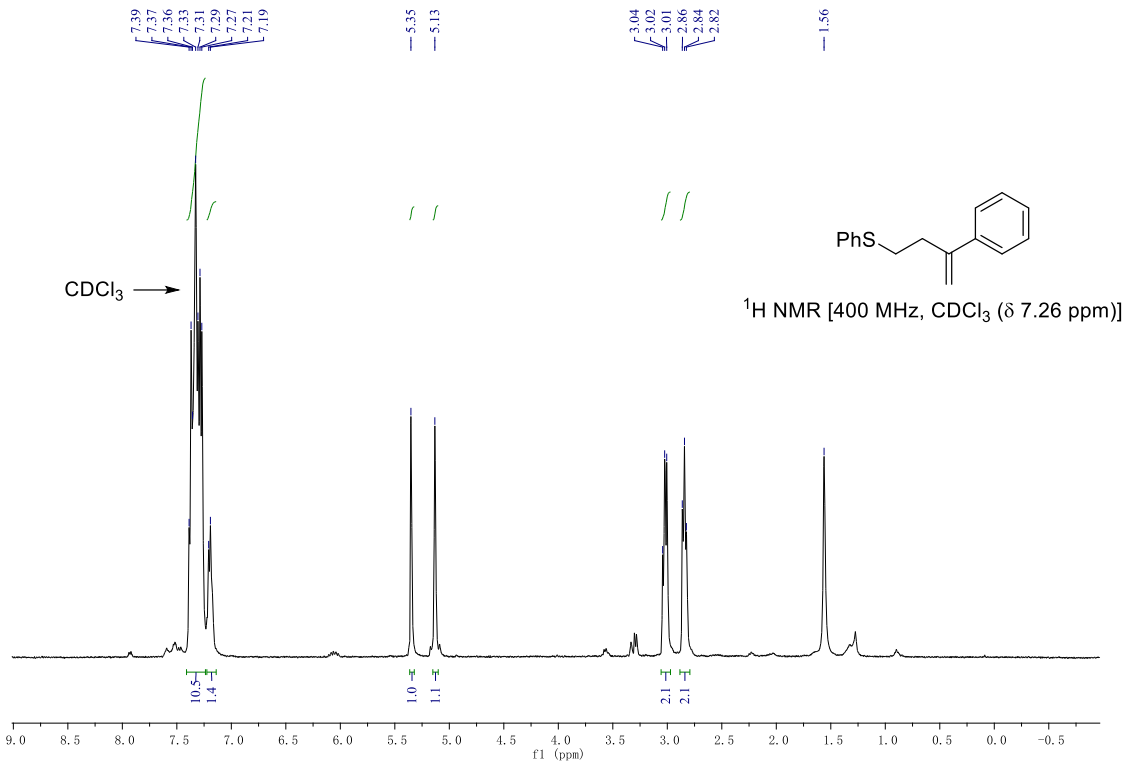


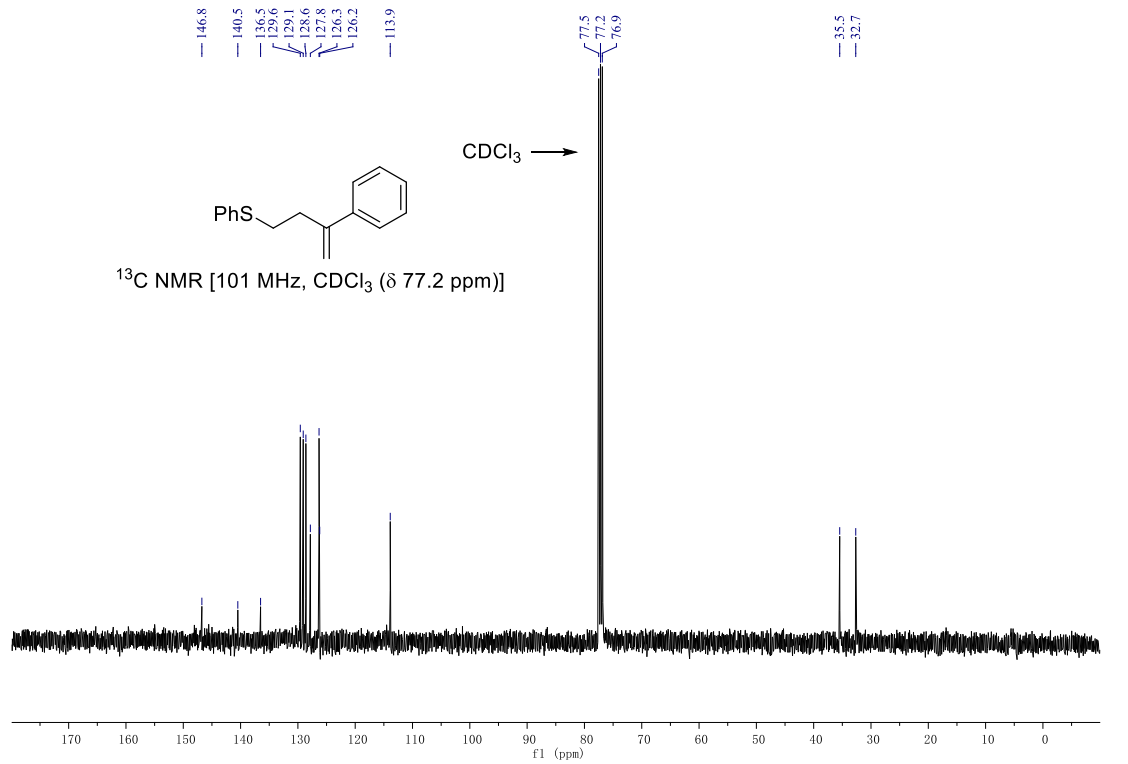
methyl *N*-acetyl-*S*-(3-methylbut-3-en-1-yl)-*L*-cysteinate (6bd)



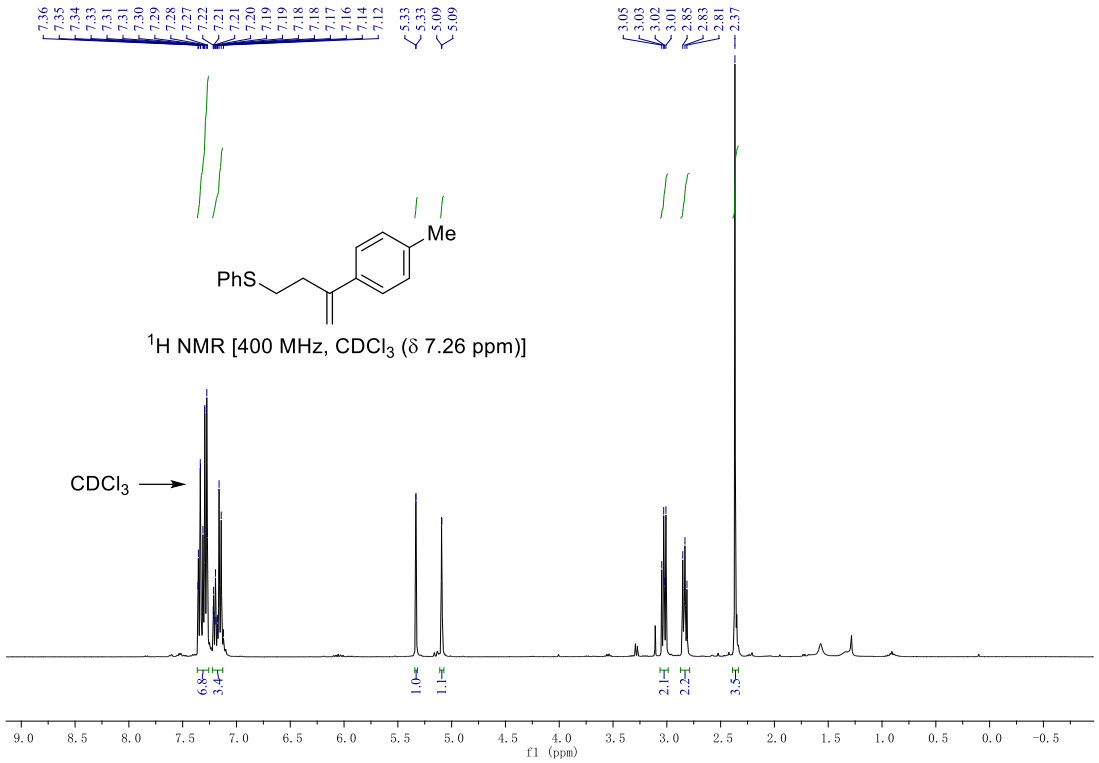


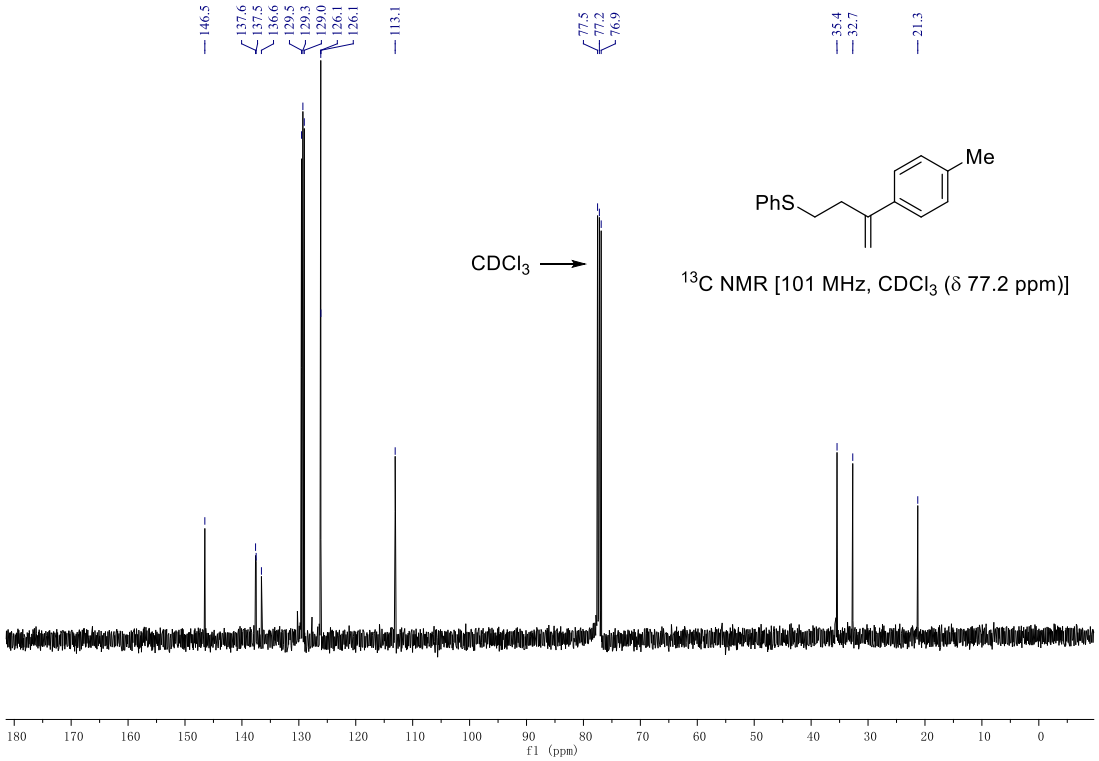
phenyl(3-phenylbut-3-en-1-yl)sulfane (6ae)



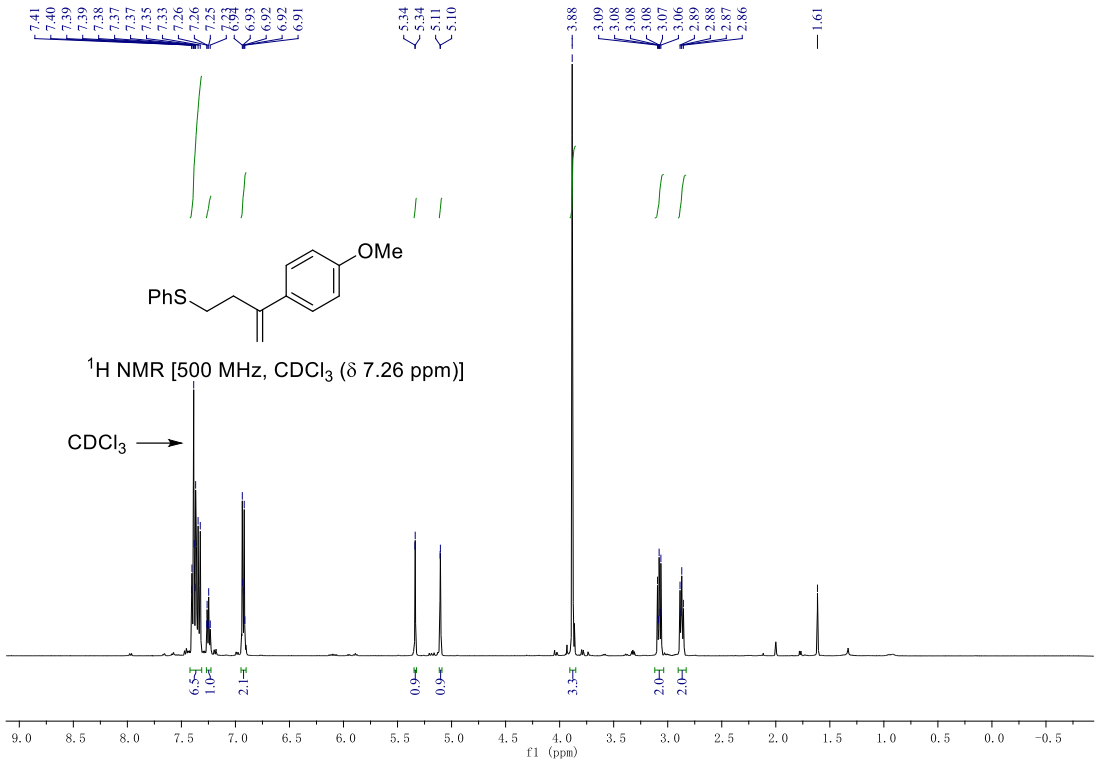


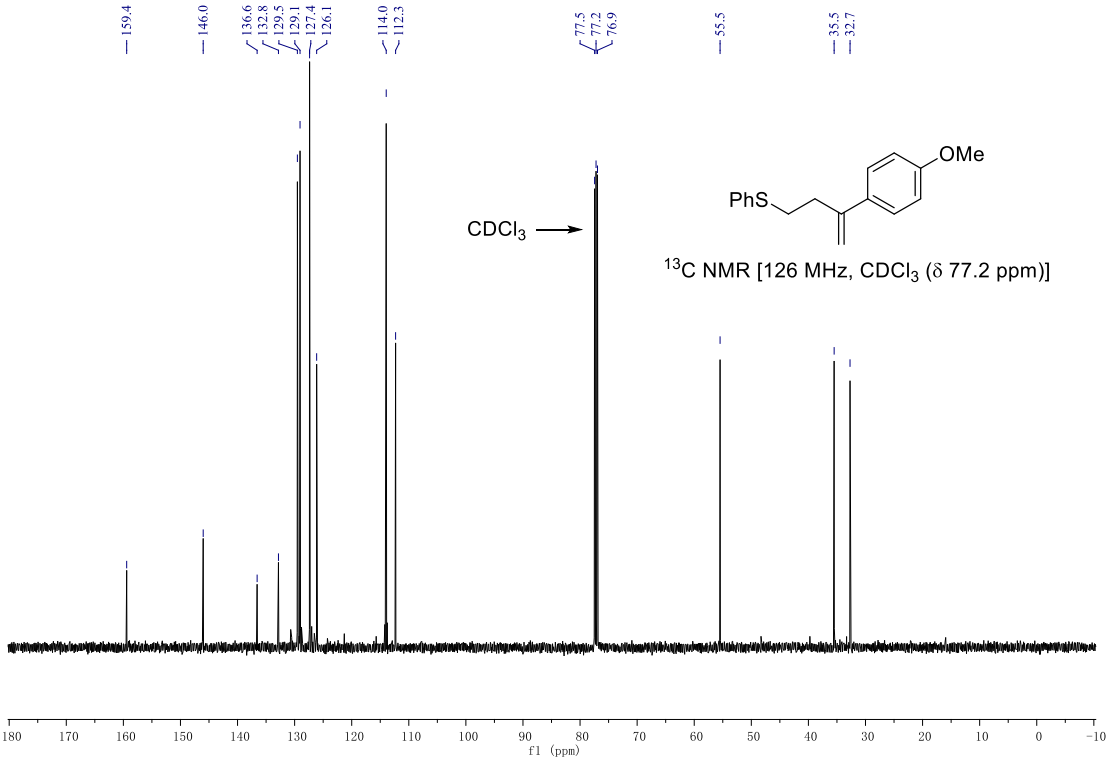
phenyl(3-(*p*-tolyl)but-3-en-1-yl)sulfane (6af)



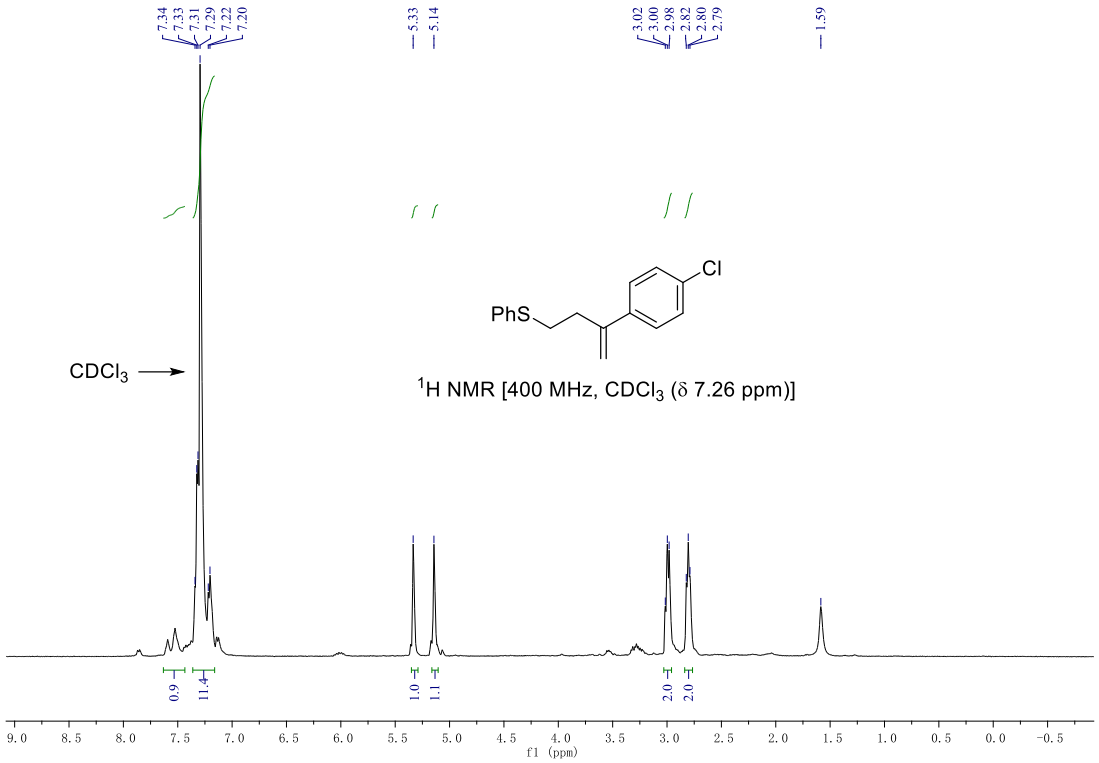


(3-(4-methoxyphenyl)but-3-en-1-yl)(phenyl)sulfane (6ag)

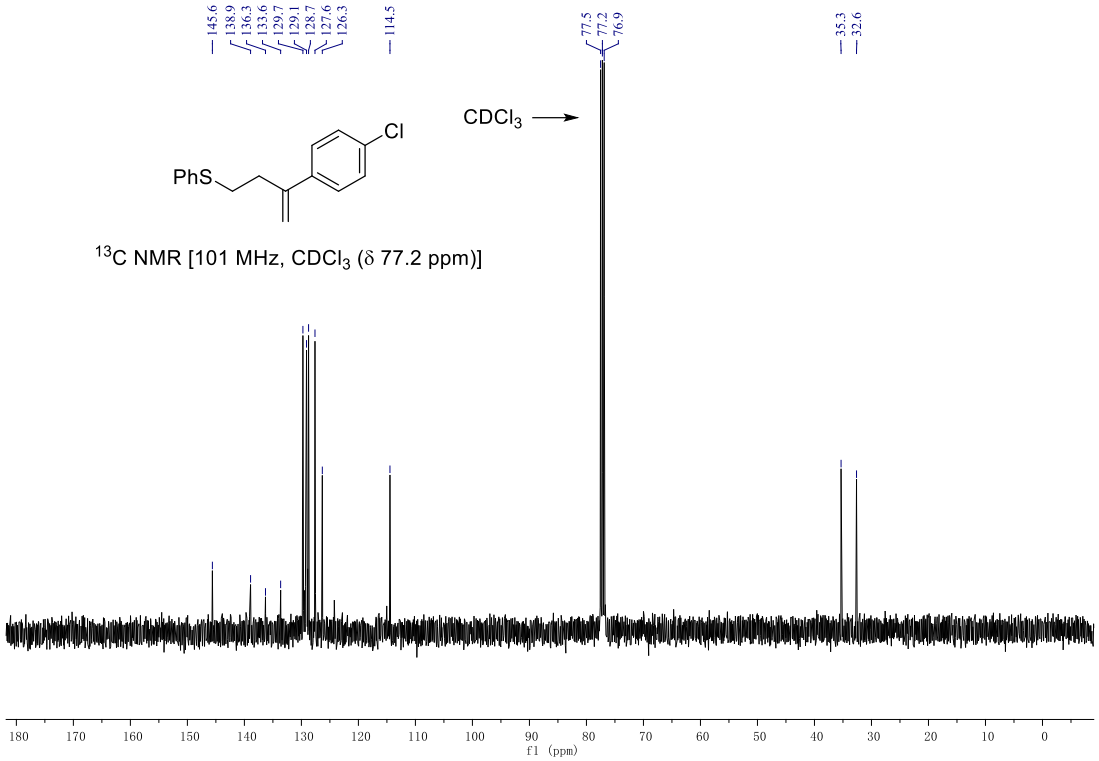




(3-(4-chlorophenyl)but-3-en-1-yl)(phenyl)sulfane (6ah)

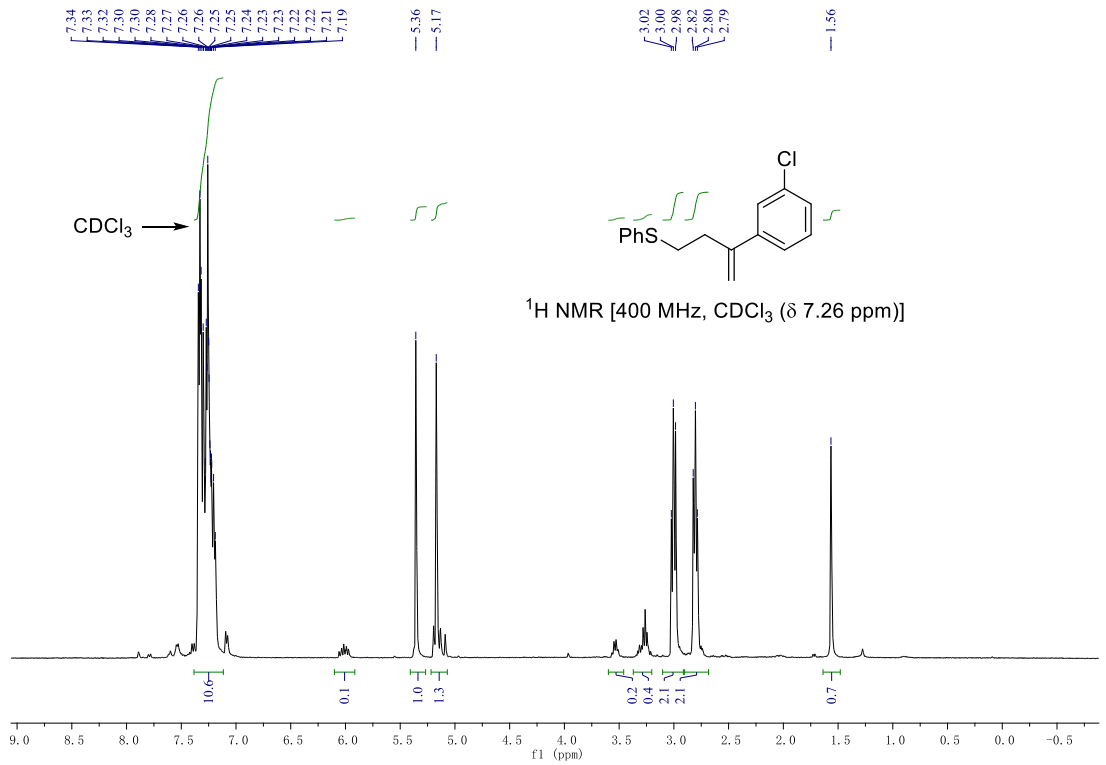


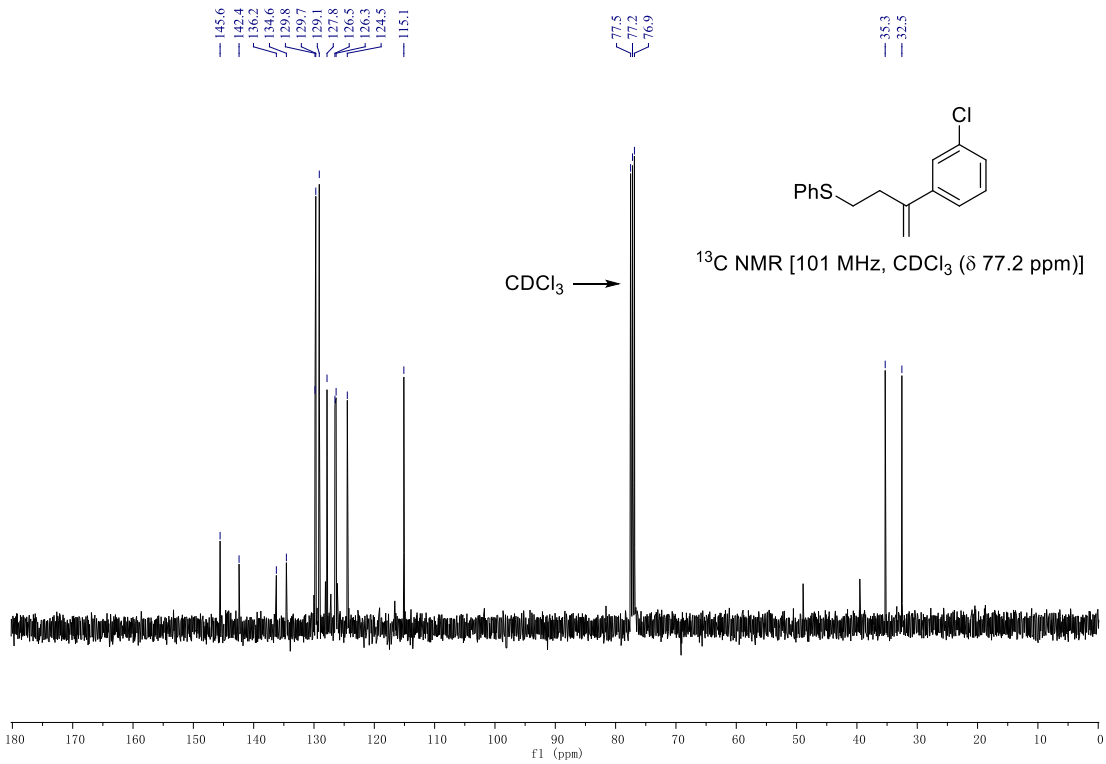
^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)]



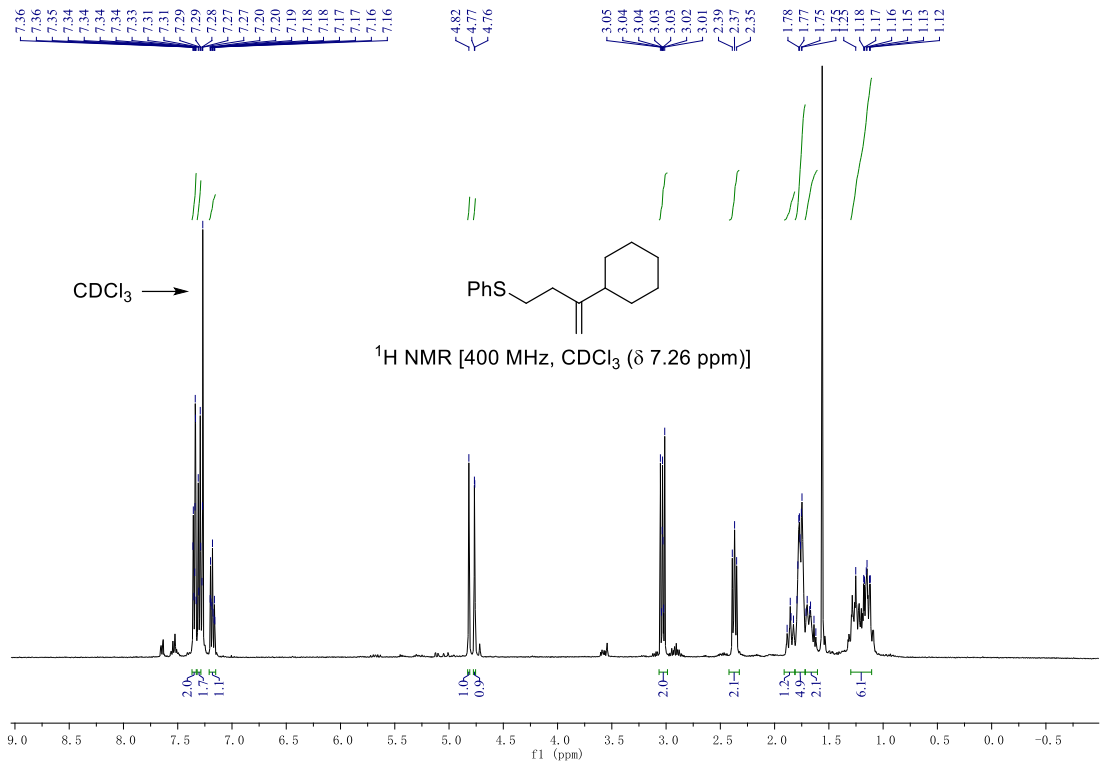
^{13}C NMR [101 MHz, $CDCl_3$ (δ 77.2 ppm)]

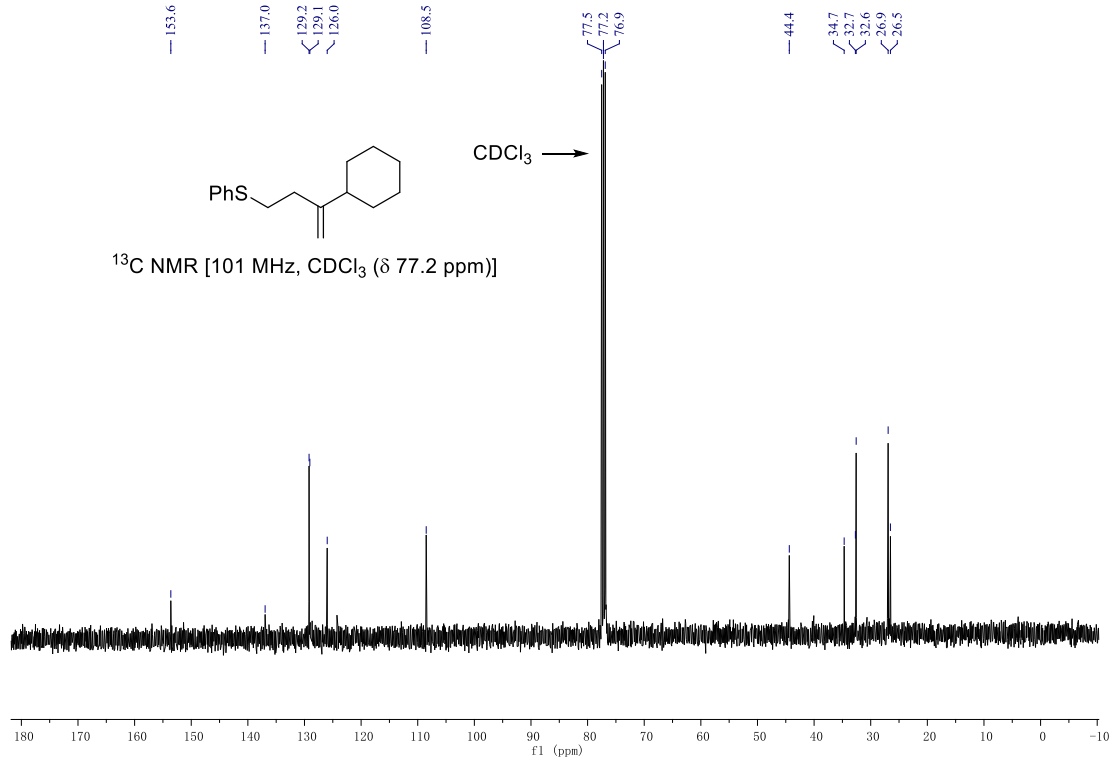
(3-(3-chlorophenyl)but-3-en-1-yl)(phenyl)sulfane (6ai)



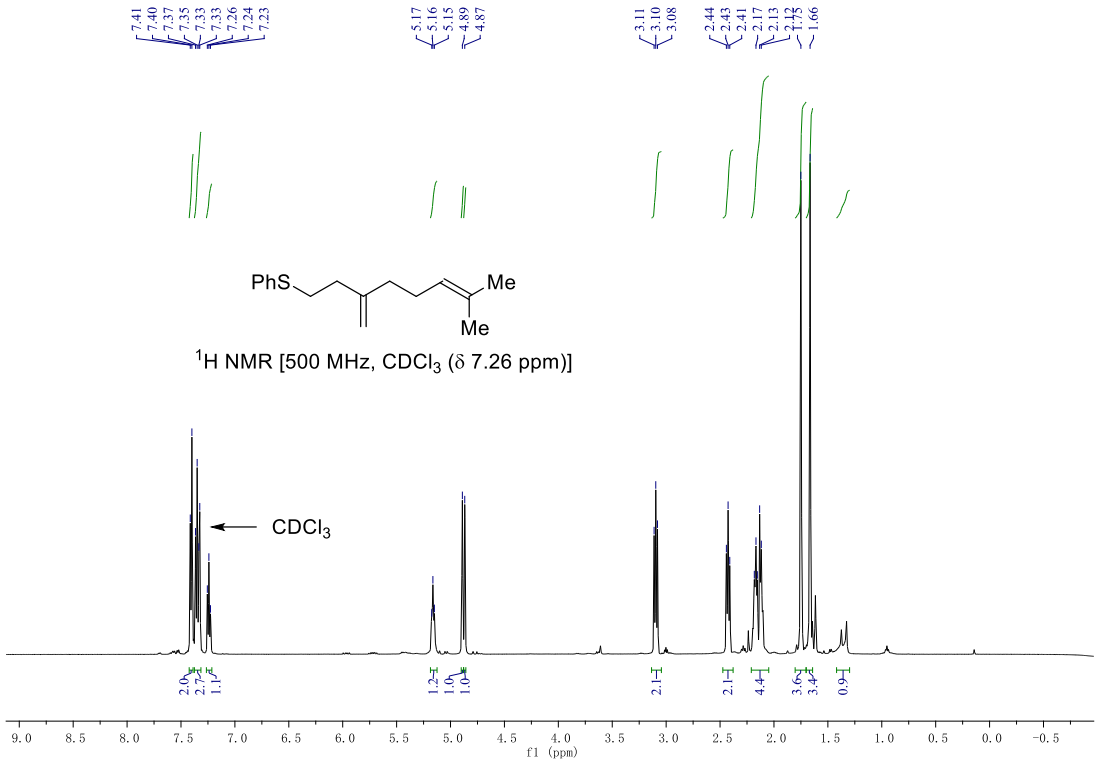


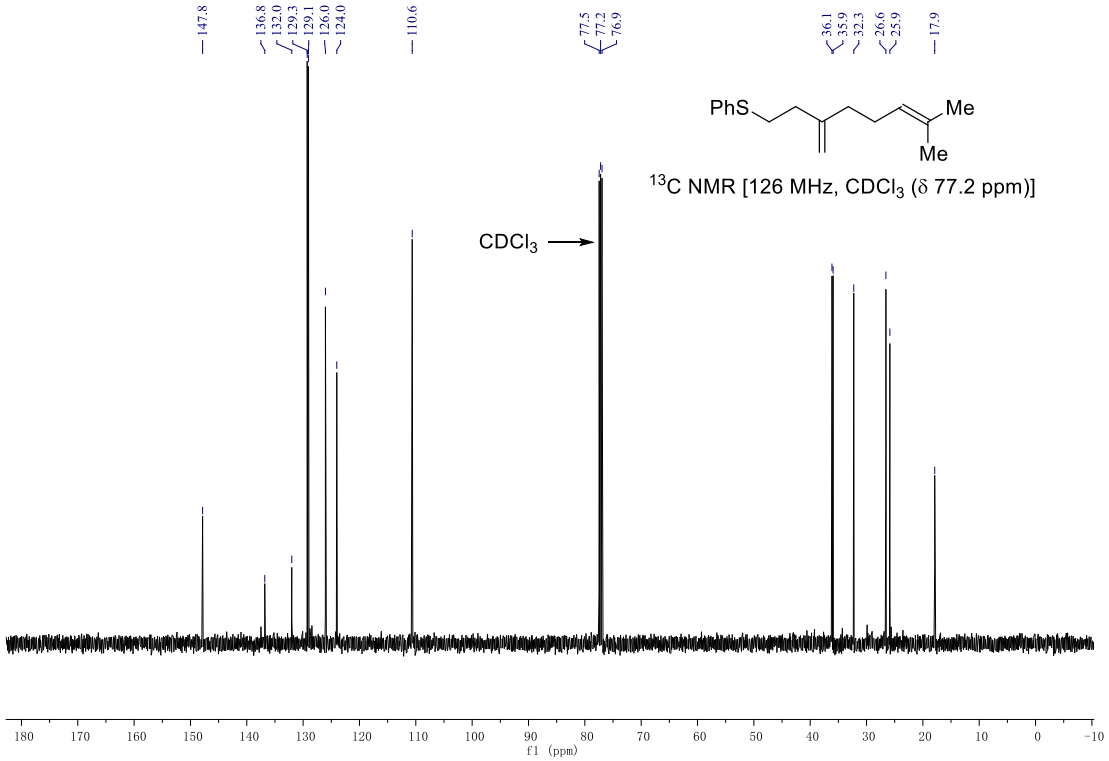
(4-cyclohexylbut-3-en-1-yl)(phenyl)sulfane (6aj)



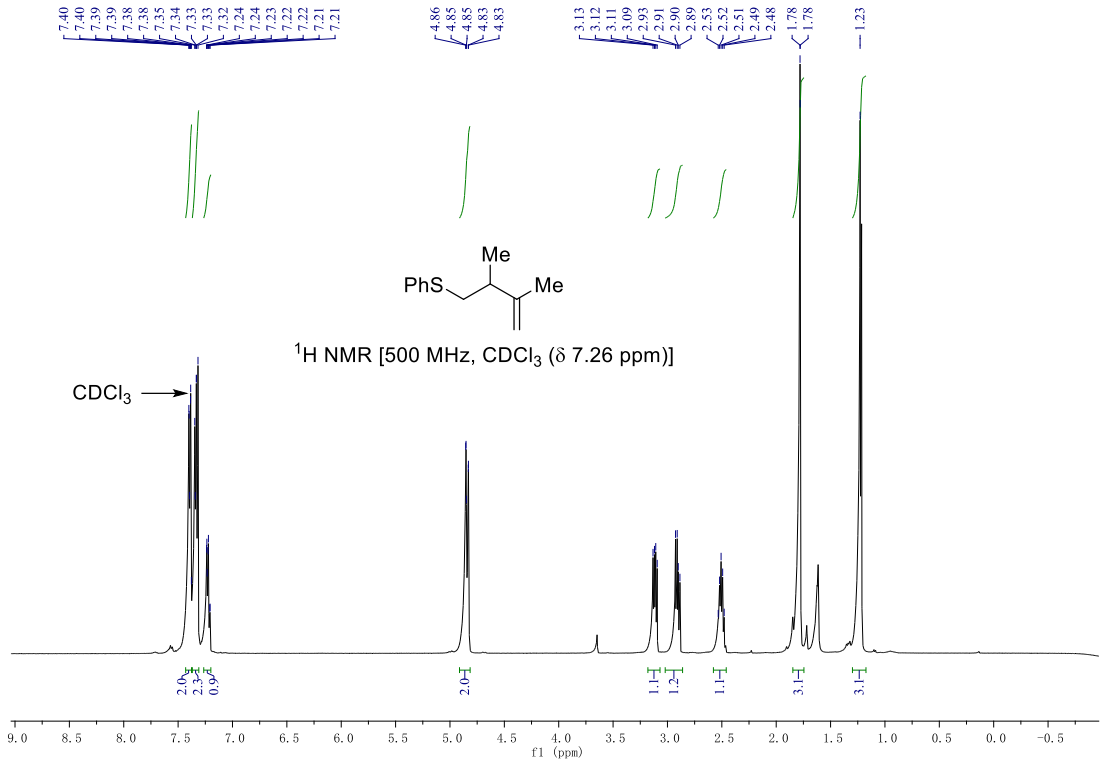


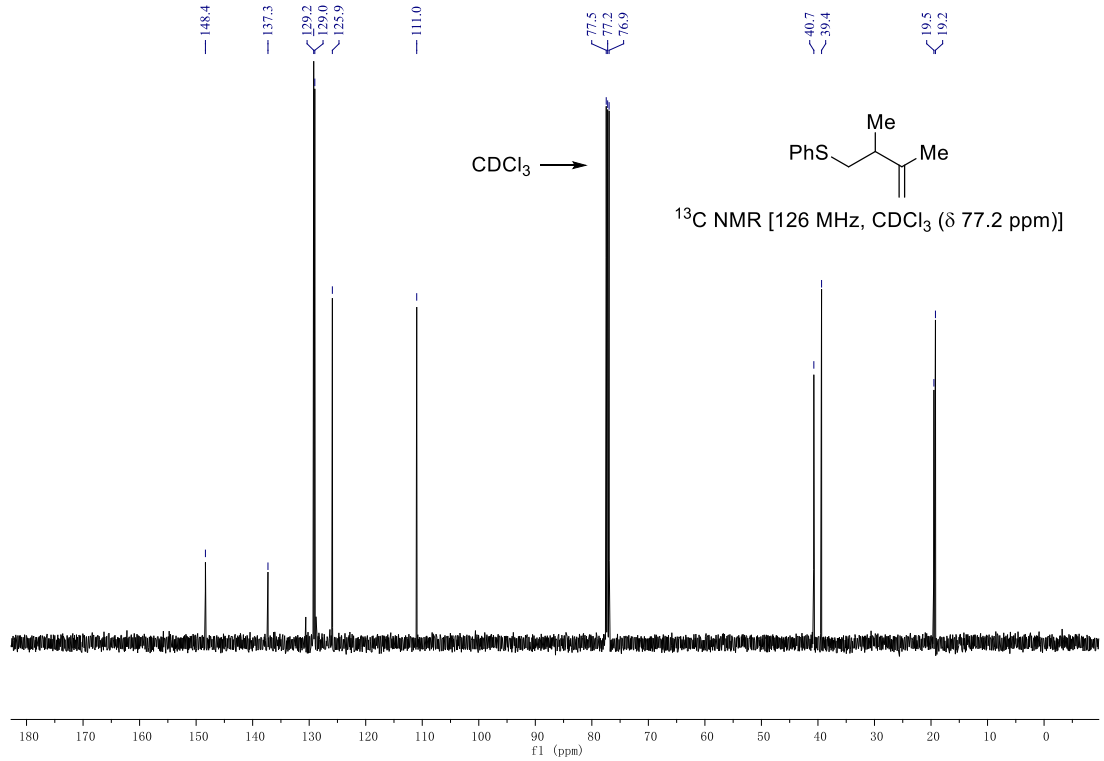
(5-methyl-3-methyleneoct-6-en-1-yl)(phenyl)sulfane (6aa)



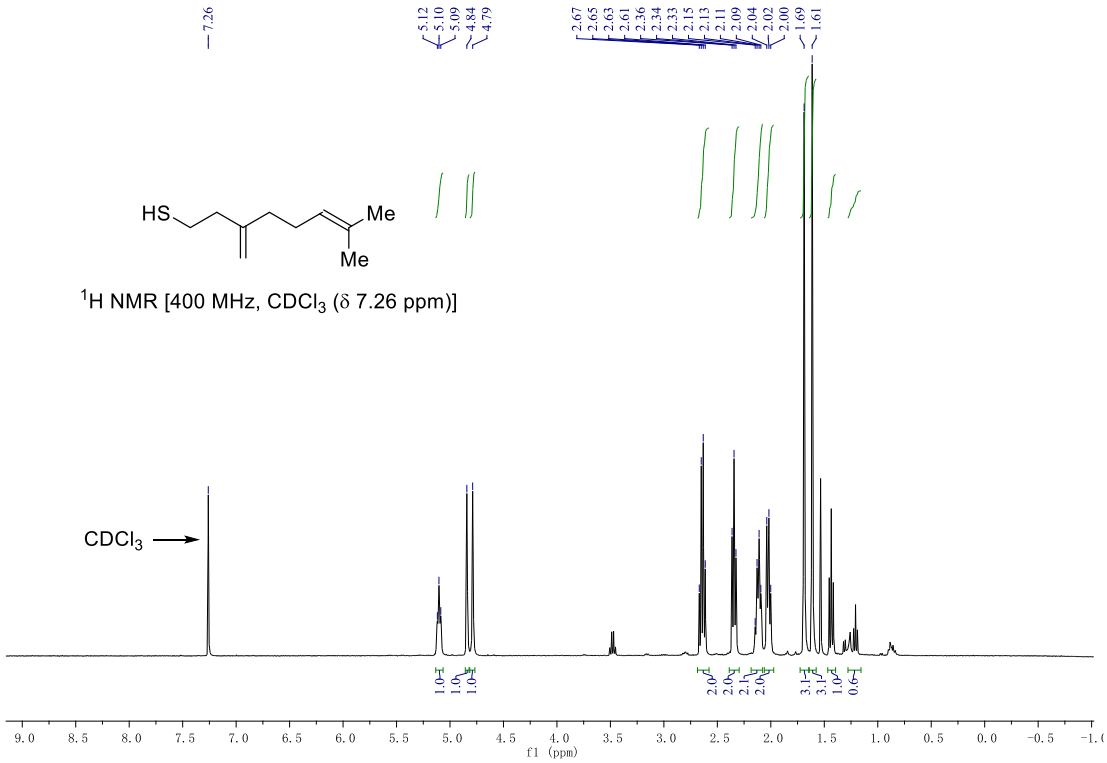


(2,3-dimethylbut-3-en-1-yl)(phenyl)sulfane (6al)

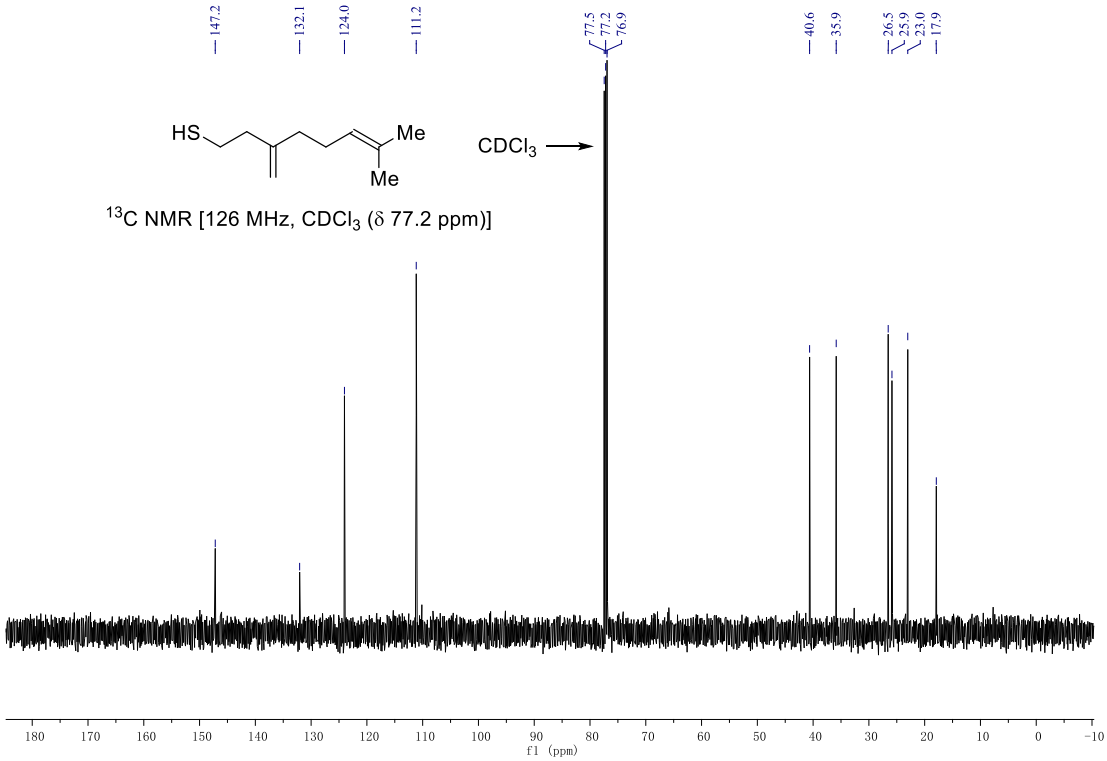




Compound 8

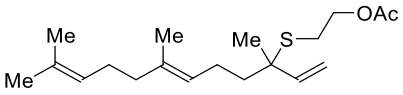


^{1}H NMR [400 MHz, $CDCl_3$ (δ 7.26 ppm)]

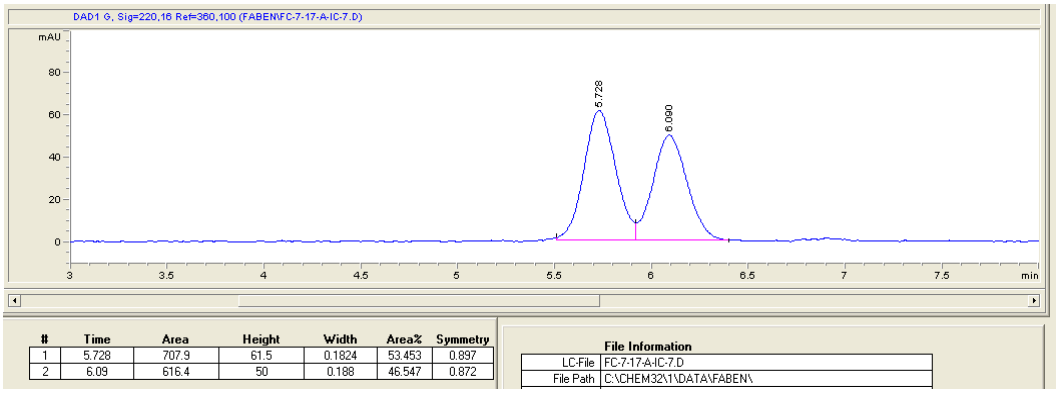


^{13}C NMR [126 MHz, $CDCl_3$ (δ 77.2 ppm)]

9. SFC spectra



***rac*-3ec**



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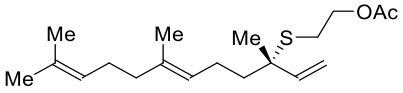

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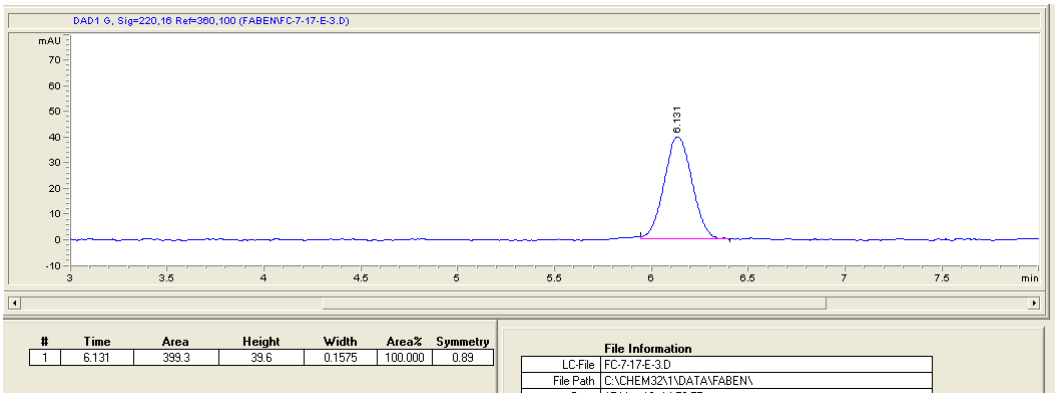

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